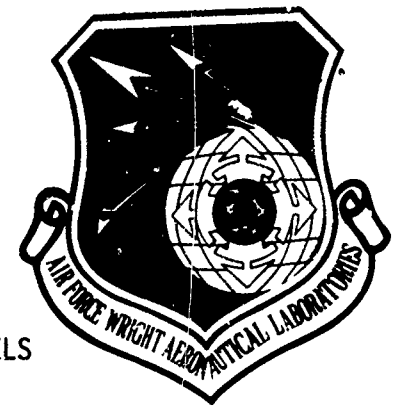
AFWAL-TR-82-2015



AD A118838

ANALYTICAL TECHNIQUES FOR AROMATIC COMPONENTS IN AIRCRAFT FUELS

J. S. Warner
T. H. Danison
J. S. McNulty

BATTELLE
COLUMBUS LABORATORIES
505 KING AVENUE
COLUMBUS, OHIO 43201

May 1982

Final Technical Report for Period 15 June 1978 --- 30 September 1981

Approved for Public Release; Distribution Unlimited

DTIC FILE COPY

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releaseable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Charlotte R. Eigel

CHARLOTTE R. EIGEL
Fuels Branch, Fuels and Lubrication Division
Aero Propulsion Laboratory

Arthur V. Churchill

ARTHUR V. CHURCHIL
Chief, Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

Robert D. Sherrill

ROBERT D. SHERRILL
Chief, Fuels and Lubrication Division
Aero Propulsion Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POSF, W-PAFB OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: AFWAL-TR-82-2015	2. GOVT ACCESSION NO.: AD-A11 8838
	3. RECIPIENT'S CATALOG NUMBER:
4. TITLE (and Subtitle): ANALYTICAL TECHNIQUES FOR AROMATIC COMPONENTS IN AIRCRAFT FUELS	5. TYPE OF REPORT & PERIOD COVERED: Final Technical Report, June 1978 - Sept 1981
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): J. S. Warner, T. H. Danison, and J. S. McNulty	8. CONTRACT OR GRANT NUMBER(s): F 33615-78-C-2019
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Program Element: 62203F, Proj/Task/Work Unit: 30480594
11. CONTROLLING OFFICE NAME AND ADDRESS: Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433	12. REPORT DATE: May, 1982
	13. NUMBER OF PAGES: 157
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

aircraft fuels	hydrocarbon type separation
aromatic hydrocarbons	nitrogen-containing compounds
gas chromatography	pyridines
ultraviolet detector	high pressure liquid chromatography
photoionization detector	mass spectrometry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An ultraviolet detector was shown to be highly satisfactory for the selective determination of aromatic components in jet fuels. The detector was operated at 208 nm and used with a fused silica capillary column gas chromatographic system. The detector gave a linear response in the range of interest and could detect individual benzenes and naphthalenes in jet fuels at levels down to 0.01% and 0.002% respectively.

Nitrogen-containing compounds were determined by the use of an alkali flame detector, high pressure liquid chromatography, and mass spectrometry.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

PREFACE

This technical report was prepared by the Analytical Chemistry Section of the Columbus Laboratories of Battelle Memorial Institute. The work described was carried out under Contract Number F-33615-78-C-2019. The program was sponsored by the Aero Propulsion Laboratory (APL), Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Program Element 62203F, Project 3048, Task 05 and Work Unit 94. The report summarizes the work performed during the period 15 June 1978 to 30 September 1981.

Dr. J. S. Warner, Battelle's Columbus Laboratories, was the Principal Investigator for the program and had the primary responsibility for the research described in this report. Mr. T. H. Danison and Mr. J. S. McNulty provided invaluable technical assistance. Mr. Paul Hayes, Jr. and Ms. Charlotte Eigel, Aero Propulsion Laboratory AFWAL/POSF were the Air Force Project Officers.

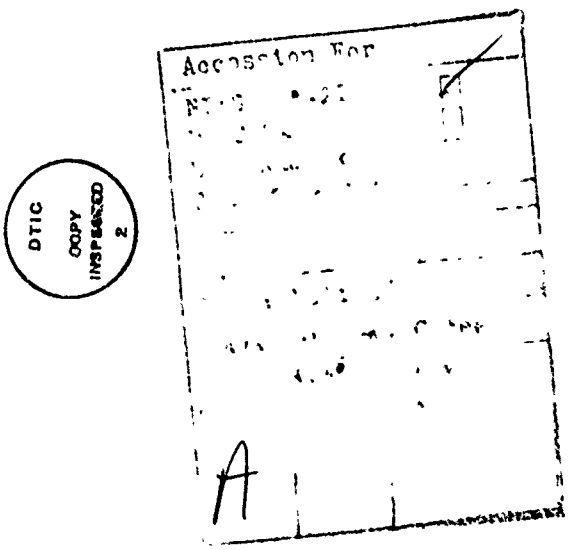


TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

Because of limitations on the supply of petroleum-based fuels, increasing amounts of alternate fuels derived from coal, shale oil, and other fossil fuels will become available and will need to be considered as sources of jet fuels. The Fuels Branch of the Aero Propulsion Laboratory is charged with developing jet fuel specifications that relate fuel chemistry to aircraft engine performance. Since the relative amounts of the individual aromatic components of a jet fuel are known to have profound effects upon the combustion properties and materials compatability of the fuel, the Air Force is very concerned about the aromatic composition of possible alternate jet fuels.

At present there is no single reliable analytical procedure available for the routine detection, identification, and quantitative determination of individual aromatic components in a fuel. The objective of the program reported here was the development of such a procedure that is both rapid and relatively inexpensive. The major emphasis was placed on the modification and evaluation of an ultraviolet detector used with a glass or fused silica capillary column gas chromatographic system. Pre-fractionation schemes, other detector systems, and spectrometric analysis methods were evaluated to determine their relative merits and to supply supportive data.

SECTION II

TECHNICAL PROGRAM SUMMARY

An ultraviolet detector (UVD) for gas chromatographic (GC) analysis was modified and evaluated for the determination of aromatic hydrocarbons in aircraft fuels. The instrumentation consisted of a Perkin Elmer Model GC-55 ultraviolet detector in which the transfer line and cell were replaced with ones designed for use with capillary columns. A 40 mm x 1.0 mm internal diameter (I.D.) glass cell was used. The effluent end of a fused silica capillary column, which also served as the transfer line, was sealed into one end of the cell. A section of fused capillary column sealed into the other end of the cell led to a flame ionization detector (FID). The system was used for the analysis of neat fuels to obtain data from both the UVD and FID simultaneously. Fifty-seven different aromatic components were quantified in 20 fuel samples using the GC-UVD.

The UVD, operated at 208 nm, was specific for aromatic compounds. No response was obtained for saturated hydrocarbons. The detection limit for benzenes in fuels was 0.01 wt % and the detection limit for naphthalenes was 0.002 wt %. The linear range was 10^3. The precision obtained was 5 to 10%.

A photoionization detector (PID) was also evaluated. The PID, using a 9.5-e.v. source, was ten times as sensitive as a UVD or FID for the detection of aromatic hydrocarbons. The selectivity of the PID provided a response for aromatic hydrocarbons that was only 40 to 200 times greater than the response for saturated hydrocarbons. The response was not as linear as that of the UVD.

Nitrogen-containing compounds in fuels were studied using a nitrogen-specific alkali flame detector (AFD), high performance liquid chromatography (HPLC), and combined gas chromatography-mass spectrometry (GC-MS) of fractions obtained by acid-base extraction and HPLC. A total of 145 different nitrogen-containing compounds, primarily pyridines and quinolines, were tentatively identified in one fuel sample.

A gas chromatographic method involving the simultaneous use of a UVD, FID, and AFD was recommended as a rapid, inexpensive, and highly informative method for the routine analysis of aircraft fuels.

SECTION III

TECHNICAL DISCUSSION

A. BACKGOUND

The major emphasis of the program involved the modification and evaluation of an ultraviolet detector (UVD) for the gas chromatographic (GC) determination of aromatic hydrocarbons in aircraft fuels. The objective was the development of a rapid method for the quantification of individual aromatic components.

The use of a GC-UVD for the direct analysis of fuels and selective determination of aromatic components was recommended by R. D. Butler (Reference 9) of Wright Patterson Air Force Base in 1974. Some of the GC-UVD design criteria provided by Butler were incorporated into a prototype constructed and evaluated by Hodgson, Tucker and Butler (Reference 11) in 1977. Concurrently a UVD designed for use in high pressure liquid chromatography (HPLC) was modified by the Perkin Elmer Corporation and offered for sale as a GC-UVD in 1977. The Perkin Elmer detector, Model GC-55, was modified and evaluated in this program.

In order to identify the components determined by a GC-UVD method, an independent qualitative analysis method is required. The method used on this program involved fractionation using adsorption column chromatography and analysis of the aromatic fraction by gas chromatography coupled with mass spectrometry (GC-MS).

The performance of other selective GC detectors was studied to determine their suitability for determing aromatic components in aircraft fuels. One of the other detectors studied was a photoionization detector (PID). Because of the lower ionization potentials of aromatic hydrocarbons relative to those of saturated hydrocarbons, the PID responds preferentially to the aromatic compounds. Another detector studied was an alkali flame detector (AFD) which is selective for nitrogen-containing compounds. Because of the importance of nitrogen-containing compounds in aircraft fuel performance, HPLC and GC-MS studies were also conducted with these compounds.

B. FRACTIONATION USING ADSORPTION COLUMN CHROMATOGRAPHY

One approach to determining the aromatic compounds present in an aircraft fuel involves the fractionation of the fuel into a nonaromatic fraction and an aromatic fraction followed by analysis of the aromatic fraction using gas chromatography (GC) or coupled gas chromatography-mass spectrometry (GC-MS). The fractionation can be accomplished by using adsorption column chromatography with silica gel, alumina, or Florisil® as the absorbent. The nonaromatic or saturated fraction can be eluted using a saturated hydrocarbon solvent such as pentane or hexane and the aromatic fraction can be eluted using a more polar solvent such as methylene chloride, benzene, or ethyl ether.

The aromatic fraction from aircraft fuels cannot be concentrated by solvent evaporation in an effort to increase the sensitivity of subsequent analyses because some of the lower-boiling components, such as benzene and toluene, would be at least partially lost. Benzene would not be suitable as an eluting solvent because benzene is a component of some aircraft fuels and the determination of small amounts of benzene in the fuels is of interest.

The fractionation of a representative aircraft fuel, a Syncrude Jet A, was studied using the different absorbents and elution solvents mentioned above. For each column chromatographic run, 32 fractions of 1.5 ml each were collected and transferred to 2-ml vials for GC anlaysis. Each fraction was analyzed using an SE-30 glass capillary column. The chromatographic patterns were entirely adequate to determine whether the components present in the fractions were saturated or aromatic.

The results obtained, given in Table 1, show that methylene chloride, benzene, and 50% methylene chloride in petroleum ether all give a sharp elution of aromatic components from saturated hydrocarbons when silica gel is used. Further dilution of the methylene chloride or benzene with petroleum ether increases the separation of saturates from aromatics but also broadens the aromatic fraction. The less polar mixtures also separate the alkylbenzenes from the alkylnaphthalenes to some extent; however, a complete separation is not needed for this program.

TABLE 1. ELUTION PATTERNS OF JET FUEL COMPONENTS

Adsorbent	Elution Solvent for Aromatics[a]	Fraction Numbers of Fractions Containing Saturated Hydrocarbons[c]	Fraction Numbers of Fractions Containing Aromatic Hydrocarbons[c]
Silica Gel	20% CH_2Cl_2 in P.E.[b]	2 to 7	21 to 25
Silica Gel	50% CH_2Cl_2 in P.E.	2 to 7	18 to 20
Silica Gel	CH_2Cl_2	2 to 7	18 to 20
Silica Gel	10% Benzene in P.E.	2 to 7	23 to 30
Silica Gel	20% Benzene in P.E.	2 to 7	20 to 25
Silica Gel	50% Benzene in P.E.	2 to 7	19 to 22
Silica Gel	Benzene	2 to 7	19 to 21
Florisil®	20% Benzene in P.E.	3 to 9	19 to 23

a. Low-boiling petroleum ether was used for the elution of saturated components in all cases.
b. Petroleum ether.
c. A sample containing 25 µl of jet fuel in 2 ml of pentane was placed on a chromatography column containing 10g of adsorbent and eluted with 20 ml of petroleum ether followed by 30 ml of the elution solvent for aromatics. Thirty-two 1.5-ml fractions, numbered 1 to 32, were collected and analyzed by GC to detect saturated hydrocarbons and aromatic hydrocarbons.

Florisil® can also be used to provide a complete separation of saturates from aromatics but the separation is not quite as sharp. Other eluting solvents were tried with Florisil® and also with alumina; however, poor separations were obtained presumably because the gravity flow rates were too high. In order to achieve good chromatographic performance with the column size used, the flow rate should be restricted to 1 to 2 ml/min. The gel nature of silica gel automatically keeps the flow rate in this range.

The recommended fractionation procedure selected as a result of the above studies involves the use of activated silica gel as the adsorbent and the use of n-pentane and methylene chloride as the elution solvents for the nonaromatic and aromatic components, respectively. The aromatic fraction obtained can be analyzed by GC or GC-MS without any further concentration. The details of the recommended fractionation procedure are given in Appendix A.

Five aircraft fuels supplied by the sponsor were fractionated using the procedure given in Appendix A. The aromatic fractions obtained were analyzed by GC and GC-MS using a 30-m x 0.25-mm SE-54 glass capillary column that achieved approximately 75,000 theoretical plates. The column oven temperature was programmed from 0 to 200°C at 2 degrees per minute.

The individual aromatic components in the samples were tentatively identified on the basis of their mass spectra and retention times. The GC-MS total ion chromatogram from the aromatic fraction of a sample of JP-4/aromatic-solvent blend, which contained most of the components present in all five jet fuel samples studied, is given in Figure 1. The mass spectral identifications or tentative identifications of 94 components found in JP-4/aromatic-solvent blend are given in Table 2.

Gas chromatograms of the aromatic fractions from the five fuel samples studied are shown in Figures 2 to 6. The component identifications are those given in Table 2. This information was used subsequently for the tentative identifications of aromatic components in neat fuel samples detected by GC analysis using an ultraviolet detector.

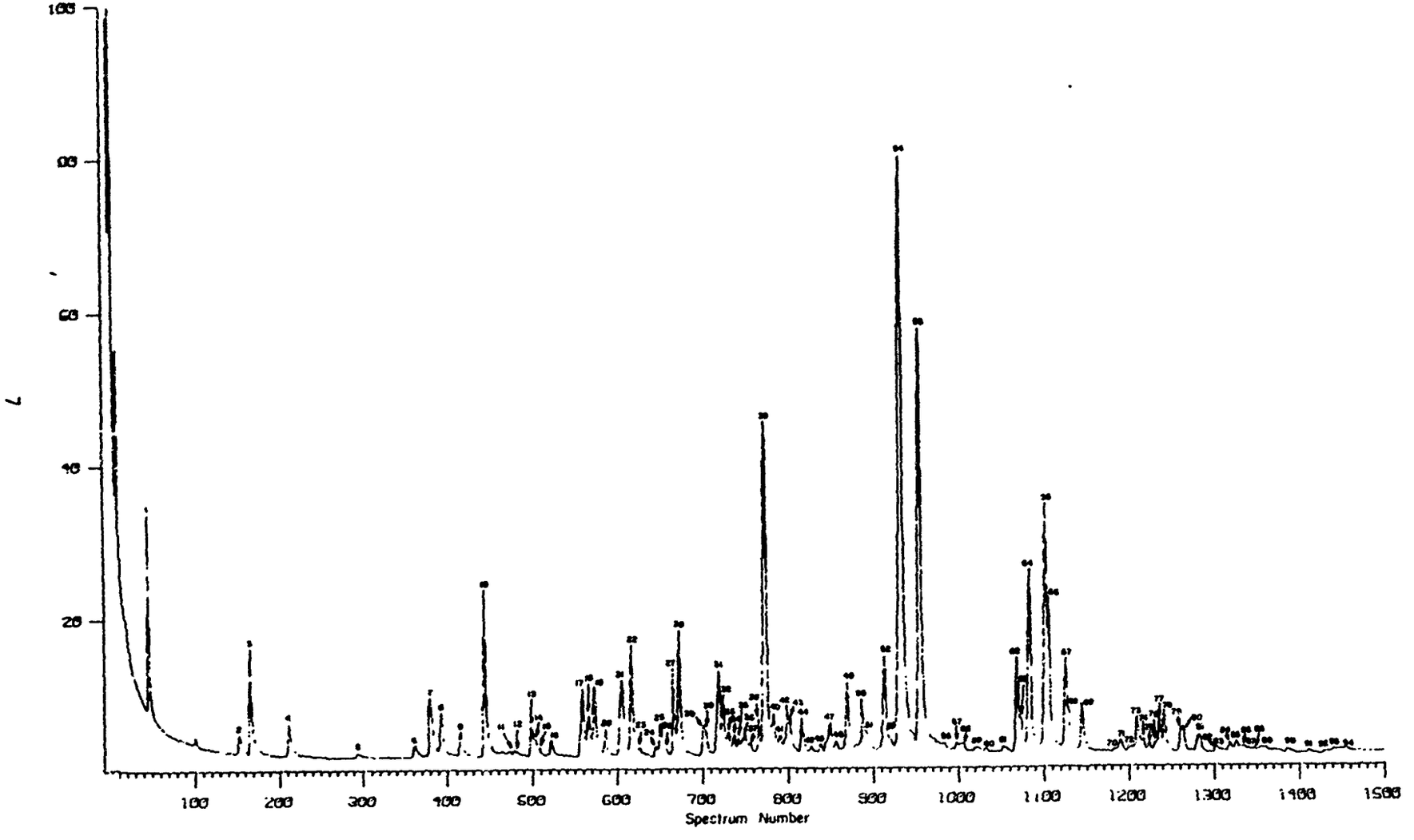


Figure 1. Total Ion Chromatogram of the Aromatic Fraction of JP-4 / Aromatic-Solvent Blend.

TABLE 2. TENTATIVE IDENTIFICATION OF AROMATIC HYDROCARBONS IN AIRCRAFT FUELS

GC Peak No.	Tentative Identification	GC Peak No.	Tentative Identification
1.	Toluene	48.	C_6-Benzene
2.	Ethylbenzene	49.	C_2-Indane
3.	m & p-Xylene	50.	C_2-Indane
4.	o-Xylene	51.	C_2-Indane
5.	Isopropylbenzene	52.	C_2-Indane
6.	Propylbenzene	53.	C_6-Benzene
7.	1-Ethyl-4-methylbenzene	54.	2-Methylnaphthalene
8.	1,3,5-Trimethylbenzene	55.	1-Methylnaphthalene
9.	1-Ethyl-2-methylbenzene	56.	C_6-Benzene
10.	1,2,4-Trimethylbenzene	57.	C_4-Indane
11.	Isobutylbenzene	58.	C_3-Indane
12.	sec-Butylbenzene	59.	C_3-Indane
13.	1,2,3-Trimethylbenzene	60.	C_3-Indane
14.	1-Methyl-4-isopropylbenzene	61.	Biphenyl
15.	1-Methyl-2-isopropylbenzene	62.	2-Ethylnaphthalene
16.	Indane	63.	1-Ethylnaphthalene
17.	1-Methyl-3-propylbenzene	64.	2,6-Dimethylnaphthalene
18.	1-Methyl-4-propylbenzene	65.	1,3-Dimethylnaphthalene
19.	1,3-Dimethyl-5-ethylbenzene	66.	1,6-Dimethylnaphthalene
20.	1-Methyl-2-propylbenzene	67.	2,3-Dimethylnaphthalene
21.	1,4-Dimethyl-2-ethylbenzene	68.	1,4-Dimethylnaphthalene
22.	1,3-Dimethyl-4-ethylbenzene	69.	1,2-Dimethylnaphthalene
23.	1,2-Dimethyl-4-ethylbenzene	70.	Acenaphthene
24.	C_5-Benzene	71.	Methylbiphenyl
25.	C_5-Benzene	72.	C_3-Naphthalene
26.	C_5-Benzene	73.	C_3-Naphthalene
27.	1,2-Dimethyl-3-ethylbenzene	74.	C_3-Naphthalene
28.	1,2,4,5-Tetramethylbenzene	75.	C_3-Naphthalene
29.	Methylindane	76.	C_3-Naphthalene
30.	C_5-Benzene	77.	C_3-Naphthalene
31.	C_5-Benzene	78.	C_3-Naphthalene
32.	1,2,3,4-Tetramethylbenzene	79.	C_3-Naphthalene
33.	C_5-Benzene	80.	C_3-Naphthalene
34.	C_5-Benzene	81.	C_3-Naphthalene
35.	C_5-Benzene	82.	C_3-Naphthalene
36.	C_5-Benzene	83.	C_2-Biphenyl
37.	C_5-Benzene	84.	C_2-Biphenyl
38.	C_5-Benzene	85.	C_4-Naphthalene
39.	Naphthalene	86.	C_2-Biphenyl
40.	C_5-Benzene	87.	C_3-Biphenyl
41.	C_5-Benzene	88.	C_4-Naphthalene
42.	C_5-Benzene	89.	C_4-Naphthalene
43.	C_5-Benzene	90.	C_4-Naphthalene
44.	C_5-Benzene	91.	C_4-Naphthalene
45.	C_5-Benzene	92.	C_4-Naphthalene
46.	C_6-Benzene	93.	C_3-Biphenyl
47.	C_5-Benzene	94.	C_3-Biphenyl

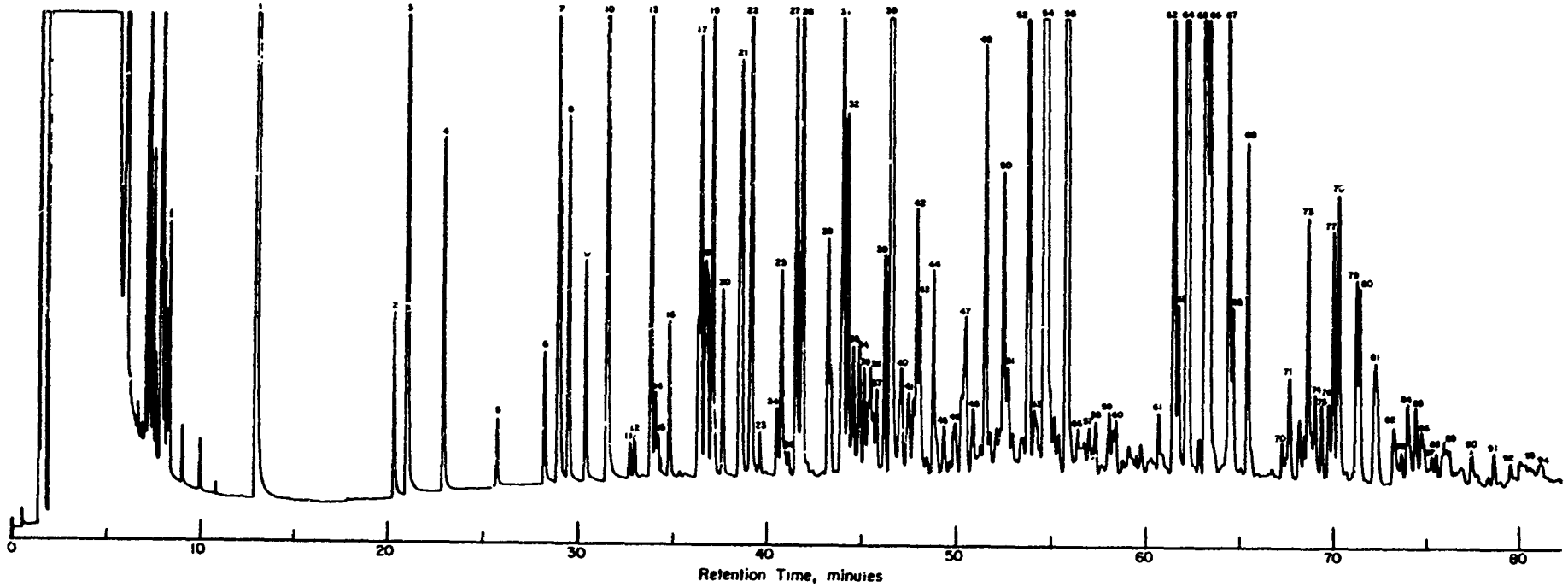


Figure 2. FID Gas Chromatogram of the Aromatic Fraction of JP-4/ Aromatic-Solvent Blend.

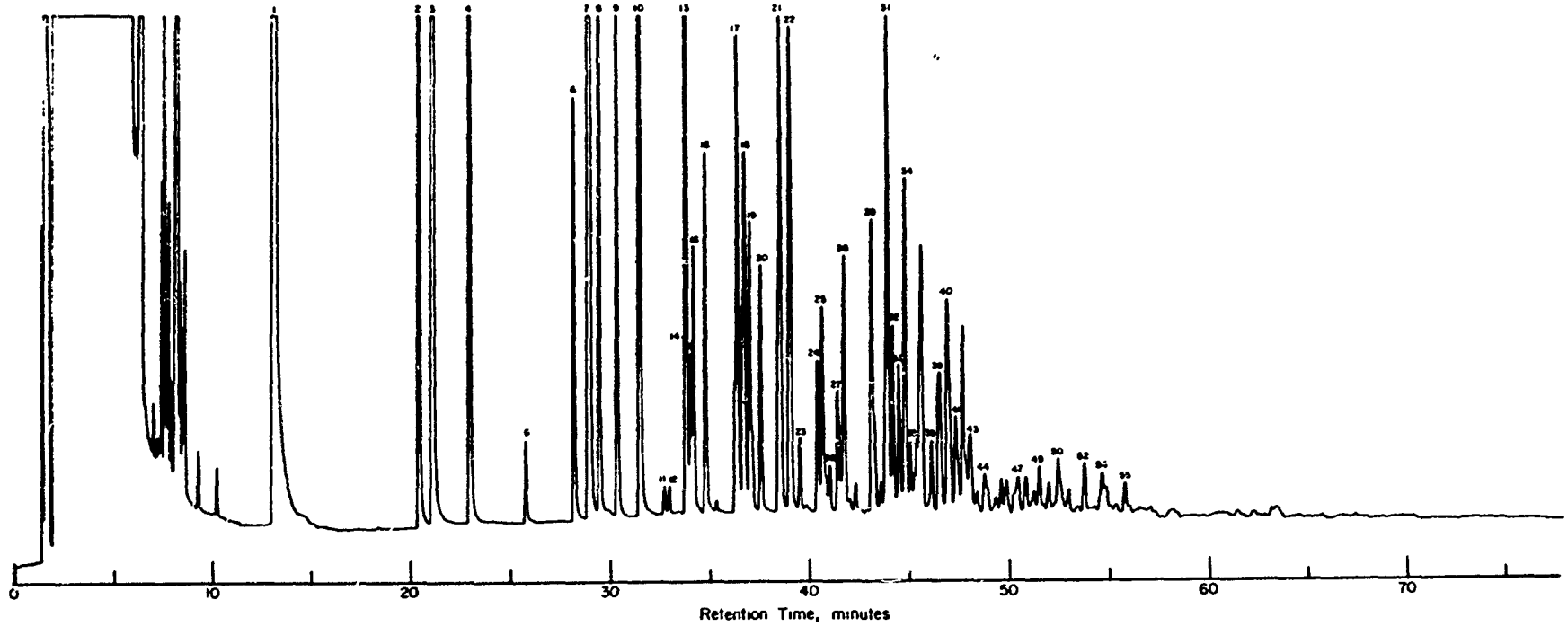


Figure 3. FID Gas Chromatogram of the Aromatic Fraction of Shale Oil JP-4.

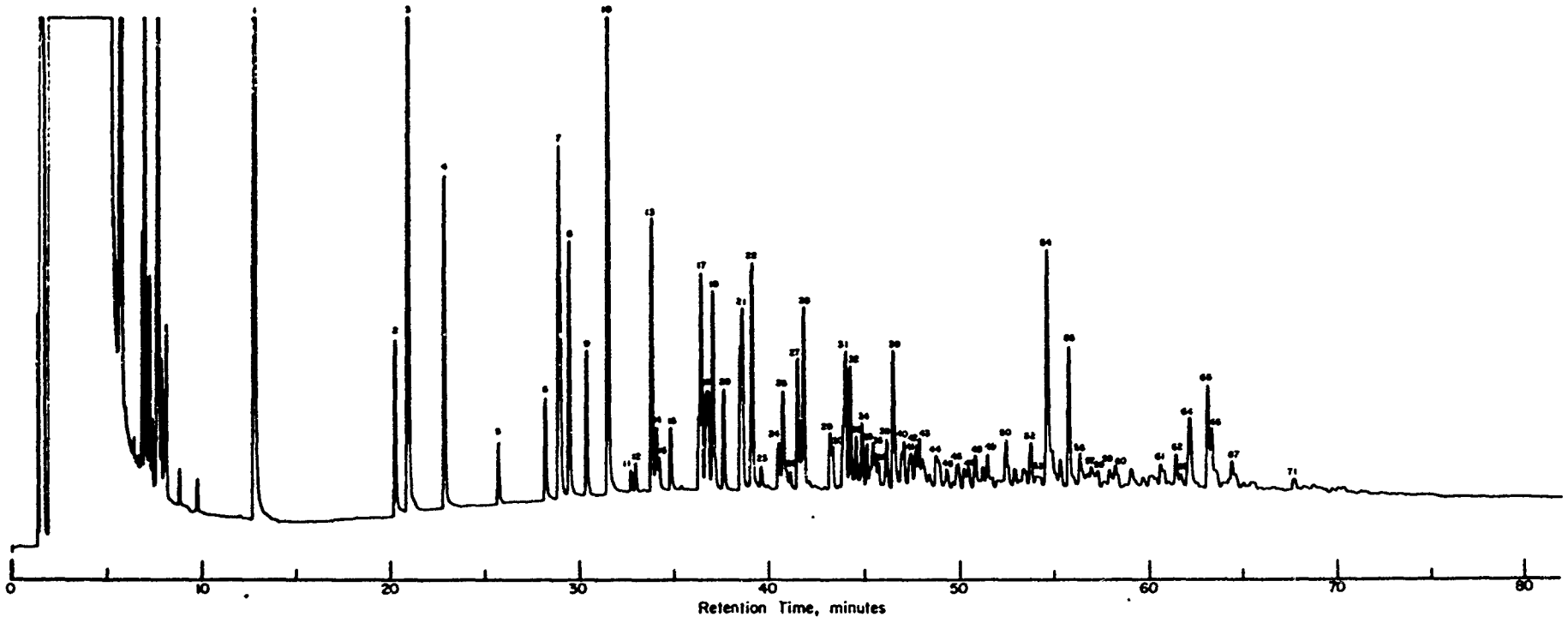


Figure 4. FID Gas Chromatogram of the Aromatic Fraction of Specification JP-4.

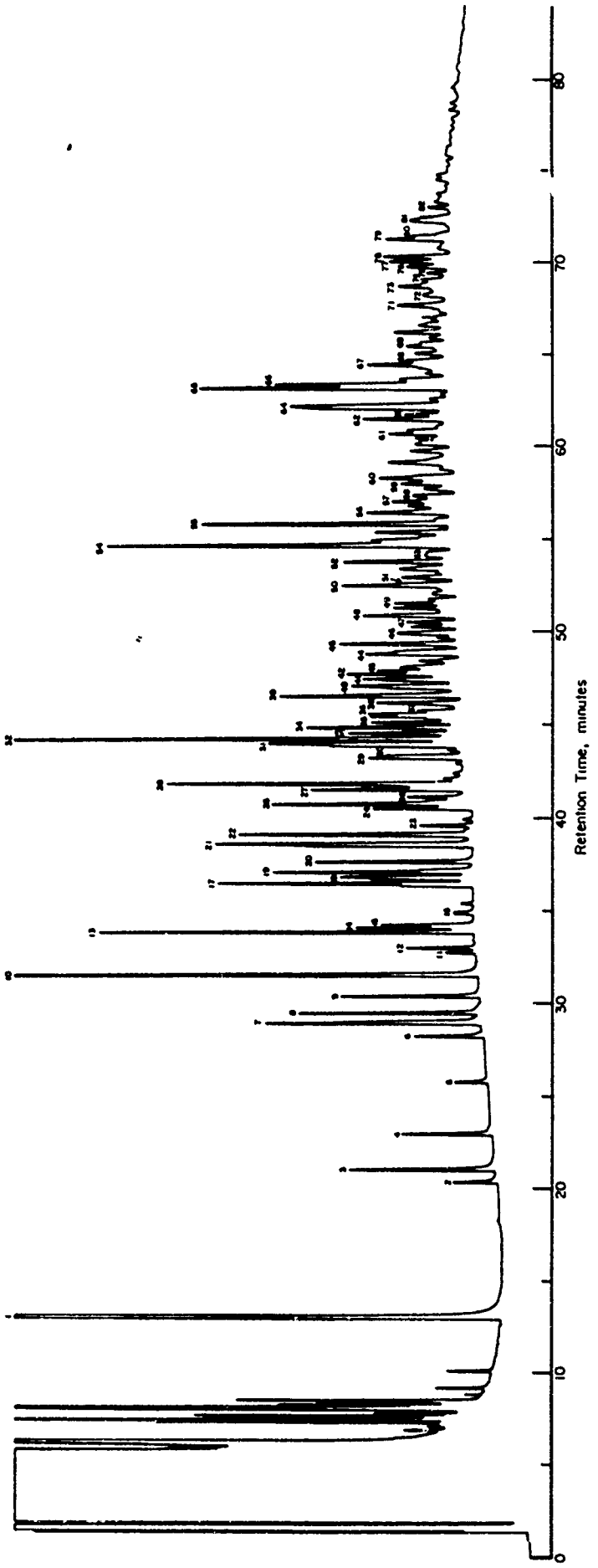


Figure 5. FID Gas Chromatogram of the Aromatic Fraction of Specification JP-8.

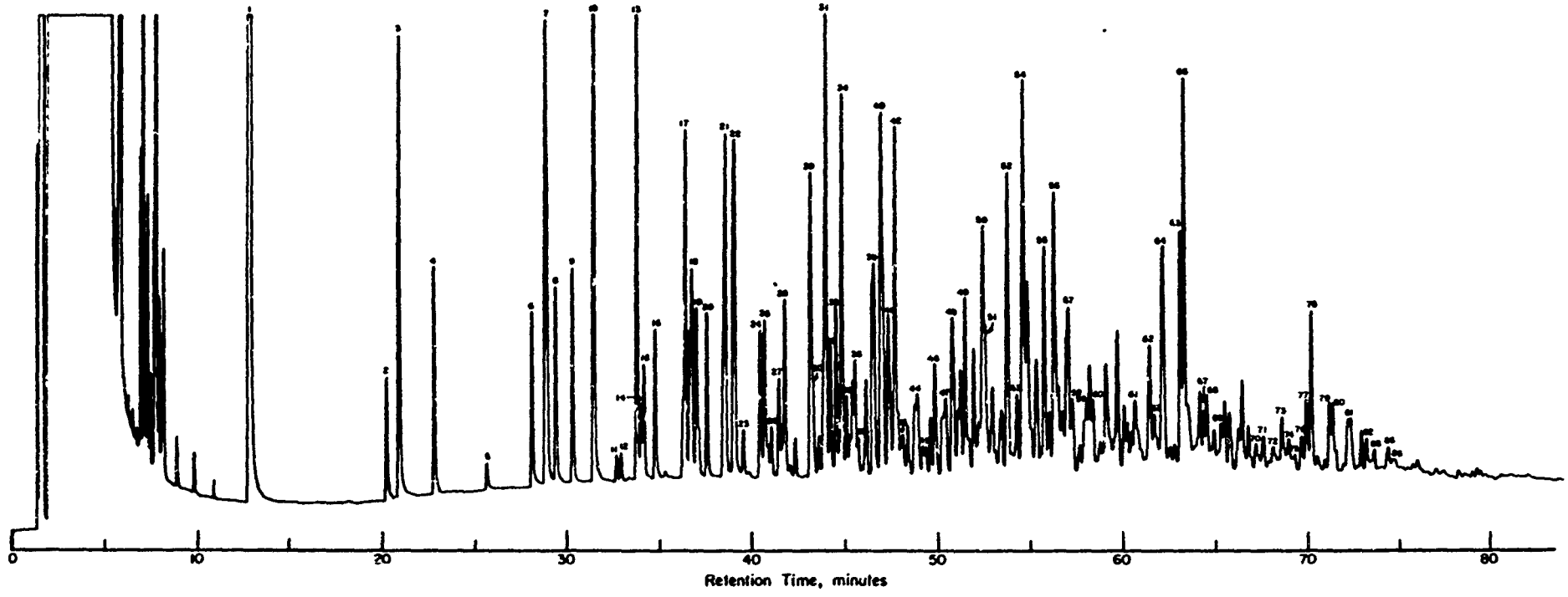


Figure 6. FID Gas Chromatogram of the Aromatic Fraction of Syncrude Jet A.

C. ULTRA-VIOLET DETECTOR STUDIES

1. Literature Search

Computerized literature searches were made of Chemical Abstracts sources for 1972 to 1981, Defense Documentation Center sources for 1952 to 1981, and National Technical Information Service sources for 1964 to 1981. The searches covered gas chromatography combined with ultraviolet detection. The pertinent references obtained are given on pages 83-85 in chronological order with a brief description.

Several approaches to the problem of UV detection of GC effluents involved scrubbing the effluent with a solvent and analyzing the solvent using a liquid flow-through cell and a UV detector designed for HPLC work (References 3, 6, 7, and 17). Other workers trap fractions sequentially eluted from a GC column and analyzed the fraction by conventional UV spectrophotometric methods (References 8, 13, and 14). The first direct GC-UVD studies were reported in 1963 and involved packed columns with relatively large cell volumes (References 1 and 2). The use of a vapor phase fluorescence detector and a second derivative UV detector using relatively large cell volumes have also been reported (References 4 and 10).

The initial impetus for the design of a GC-UVD system suitable for the direct selective determination of aromatic hydrocarbons in jet fuels was provided by the design criteria of Butler at Wright-Patterson Air Force Base in 1974 (Reference 9). A prototype GC-UVD was constructed and evaluated by Hodgson, Tucker, and Butler (Reference 11). Concurrently an HPLC-UV detector was modified by The Perkin-Elmer Corporation for use as a GC detector and offered for sale in 1977. Perkin-Elmer, in cooperation with Novotny and Schwende at Indiana University published two reports on the application of the detector (References 15 and 16). The use of a GC-UVD for the determination of aromatic hydrocarbons in jet fuels has also been reported by Russian workers (Reference 12).

2. Objective

The objective of the ultraviolet detector studies was the optimization of a workable ultraviolet detector for gas chromatography that would meet or exceed the following specifications.

1. Sensitivity - sufficient to detect 0.01 weight percent of toluene in an injected sample when used with an open-tubular capillary column.
2. Linear dynamic range - 10^4
3. Wavelength range - manually tunable from 220 to 650 nm.
4. Wavelength accuracy - $\pm$ 1 nm
5. Wavelength repeatability - $\pm$ 0.5 nm
6. Temperature control - variable from ambient to 300°C, accurate to $\pm$ 1°C.
7. Output level and stability - suitable for interfacing with standard laboratory recorders, integrators, and on-line data processors.
8. Micro-volume flow cell - readily accessible for cleaning and/or replacement without difficult realignment; constructed of chemically inert materials.
9. Dead volume - minimum to guarantee efficient connection to open tubular capillary columns.
10. Safety - no hazards when operated properly.

3. Instrument Modifications

A Perkin-Elmer GC-55 ultraviolet detector was purchased for evaluation as a gas chromatographic detector that would selectively detect aromatic hydrocarbons in aircraft fuels. The GC-55 uses a grating spectrophotometer with a deuterium arc source that gives a 2 mm x 6 mm image. The detector meets the wavelength range, wavelength accuracy, wavelength repeatability, temperature control, and output level and stability specifications listed above. The detector was supplied with a 1.2 m x 1.0 mm I.D. stainless steel transfer line and a 2.4 mm I.D. x 1-cm stain-

less steel flow-through cell having a volume of 45 µl. The detector is designed for use with packed GC columns. Modifications were made in the transfer line and cell in an effort to maximize the detector sensitivity for use with high-resolution glass or fused silica capillary columns. The modifications resulted in a system that was capable of detecting 0.01 weight percent of toluene and 0.002 weight percent of naphthalene in an injected fuel sample. The modifications also permitted a flame ionization detector to be connected in series with the ultraviolet detector without any loss of chromatographic resolution.

The sensitivity of an ultraviolet detector is directly related to the concentration of the analyte in the cell and the path length of the light passing through the cell. The concentration of the analyte in the cell is related to the width of the GC peak and the volume of the cell. The cell volume should be such that it can be completely filled by that portion of an eluting GC peak that has a height of at least half the maximum peak height. This maximum cell volume can be calculated by multiplying the carrier gas flow rate by the peak width at half height. Thus, if the carrier gas flow were 1.2 ml/min and the peak width at half height were 2.0 seconds, the cell volume should be no greater than 40 µl. The cell width or path length should be as long as possible. However, with a given maximum cell volume established, a longer path length requires a smaller cell diameter. The smaller the cell diameter the more difficult it is to focus an adequate amount of radiation through the cell. A practical minimum cell diameter for use with the GC-55 optics was found to be about 1.0 mm when a cell length of 4 cm was used. These dimensions give a cell volume of 31 µl.

In order to retain as much of the resolving ability of a capillary column as possible it is necessary to minimize any dead volume in the system. One approach is the use of makeup gas to sweep the GC effluent through the cell more quickly; however, the sensitivity obtained is decreased by the dilution that occurs. Instead of using makeup gas, the dead volume was minimized by eliminating the use of a union, by decreasing the diameter of the transfer line and by using a small diameter cell.

Because of concern about possible adsorptive effects of stainless steel that might lead to peak tailing, all contact of the sample with

stainless steel was eliminated. An all-glass cell having an internal diameter of 1.0 mm and a length of 40 mm was fabricated from heavy-wall borosilicate glass capillary tubing. Inlet and exit holes were drilled into each end of the cell at an angle using an ultrasonic technique. A 30-m x 0.25-mm I.D. SE-30 fused silica capillary column was used for the GC column. The effluent end of the fused silica column served as the transfer line and was attached to the inlet end of the glass cell using silicone sealant. A section of fused silica capillary was similarly sealed into the exit end of the glass cell and attached to a flame ionization detector (FID) by means of a tee that permitted the required flow of makeup gas to be introduced.

Quartz windows were fitted onto each end of the cell and silicone gaskets were used to prevent leakage. A heated aluminum block cell holder was designed that would permit the cell to be moved in any direction for alignment purposes. A drawing of the cell assembly and cell holder is given in Figure 7. A 1-in. x 1/4-in. O.D. cartridge heater was used to heat the block. The block was encased with 1/2-in. Fiberfrax® for thermal insulation. The fused silica capillaries extending from the GC oven to the cell and from the cell to the flame ionization detector were passed through a 3/16-in. copper tube that was heated with a chromel-alumel heater and jacketed with asbestos for thermal insulation.

The completed assembly had no significant dead volume or absorptive sites. No detectable loss of chromatographic resolution occurred between the ultraviolet detector and the flame ionization detector operated in series.

The flexibility of the fused silica capillary tubing used imparts a reasonable degree of ruggedness to the installed cell assembly. The assembly of the cell is not complicated but must be done carefully. Instructions for assembling and aligning the cell are given in Appendix B.

4. Response Versus Wavelength

The ultraviolet detector response obtained for an aromatic hydrocarbon is directly proportional to the absorptivity or extinction coefficient

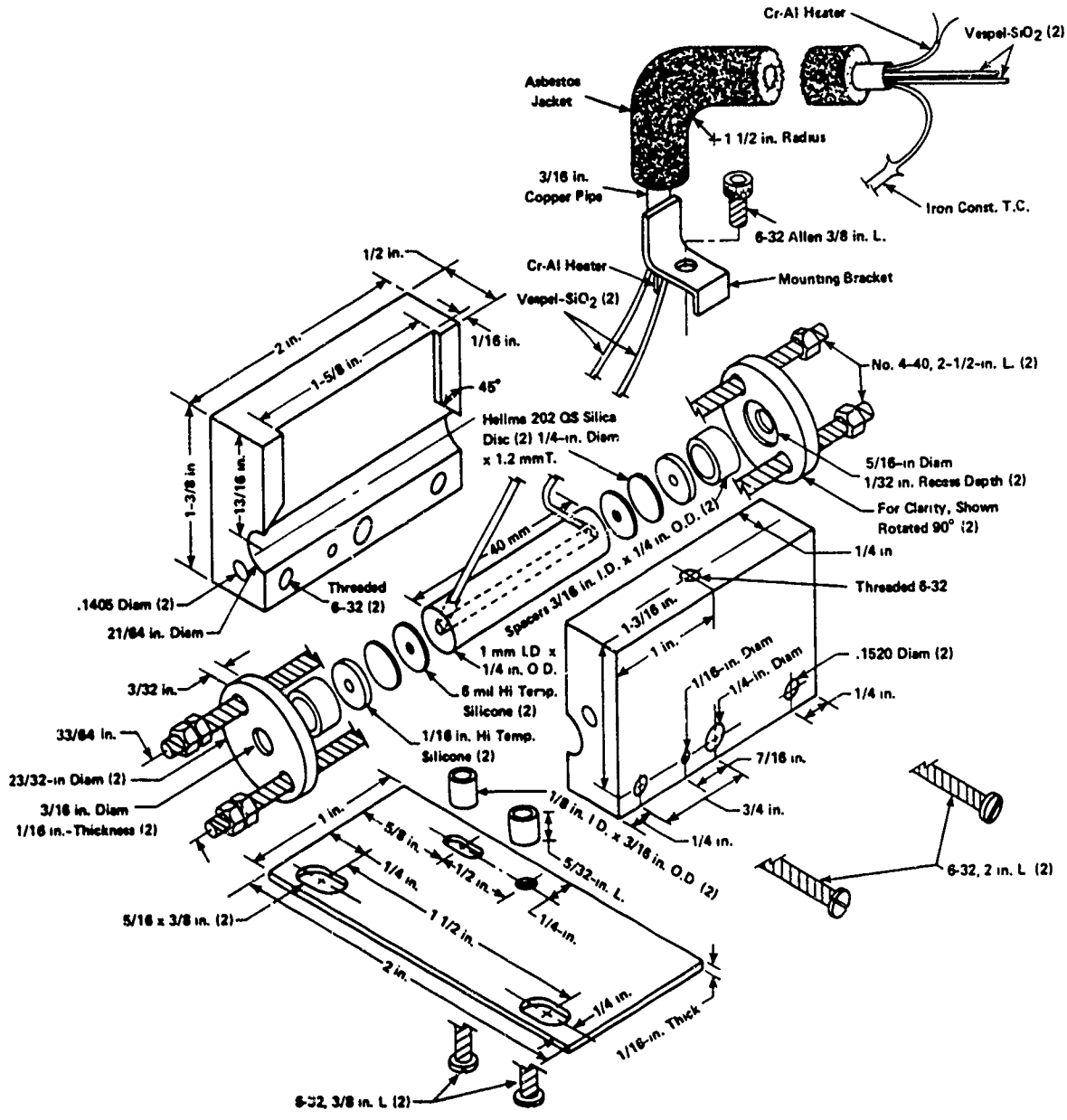


Figure 7. UV Detector Cell Assembly and Holder.

at the particular wavelength used. Although very little information is available on the gas-phase ultraviolet absorption spectra of the compounds of interest, solution-phase spectra have been compiled and should serve as useful guides in the selection of an optimum wavelength. The two major classes of aromatic hydrocarbons in aircraft fuels are benzenes and naphthalenes. In general the extinction coefficients for naphthalenes are about ten times greater than those for benzenes. The ultraviolet absorption spectra for 1,2,4-trimethylbenzene and naphthalene in hexane are shown in Figures 8 and 9, respectively. Although aromatic compounds are frequently monitored at 254 nm, it is apparent from the spectra that greater sensitivity should be achievable at 200-220 nm.

A systematic study was made of the ultraviolet detector response of 22 aromatic hydrocarbons over the range of 208 nm to 260 nm at 4 nm intervals. A 30 m x 0.25 mm I.D., SE-30 WCOT glass capillary column was used for this study. The compounds were dissolved in petroleum ether and 2 µl was injected using a split ratio of 10:1. The column temperature was programmed from 40 to 200°C at 4°C per minute. The results are given in Table 3. All runs were made in duplicate several days apart. The absolute responses from the duplicate runs usually agreed within 20%. The relative responses generally agreed within 10%. All relative responses are relative to that of an equal weight of 1,2,4-trimethylbenzene at 208 nm.

The variations of response versus wavelength are shown graphically for some of the representative hydrocarbons in Figure 10. Although the response for some of the compounds, e.g. 2,6-dimethylnaphthalene and phenanthrene, is greater at various wavelengths higher than 208 nm, the predominant aromatic hydrocarbons in jet fuel, namely the alkylbenzenes, are best detected at 208 nm. In order to avoid possible interference from nonaromatic compounds, lower wavelengths were not used. A wavelength of 208 nm was selected for subsequent evaluations. Gas chromatograms of the standard mixture at three representative wavelengths are given in Figures 11 to 13.

1,2,4-Trimethylbenzene (Pseudocumene) 1,2,4-Trimethylbenzol (Pseudocumol)		02/9 30 000/00 223
Spectrometer Spektrometer Zeiss M40 III, PMQ II (N_2 flushed)	Solvent Lösungsmittel Hexane	Formula Formel C_9H_{12}
Spec. resn Spek Auflösung 40–50 cm^{-1}	Concn Konz. $1{\cdot}26 \times 10^{-4}$, $1{\cdot}26 \times 10^{-3}$, $1{\cdot}26 \times 10^{-2}$ M	Mol wt Mol Gew 120·2
		b.p. 169°
Cell length Schichtdicke 0·1, 1·0 cm	Purity Reinheit Dist.	LR 212
G. Vagt, H. Bruns: Inst. org. Chem., Abt. Molekülspektroskopie, T. H. Braunschweig		

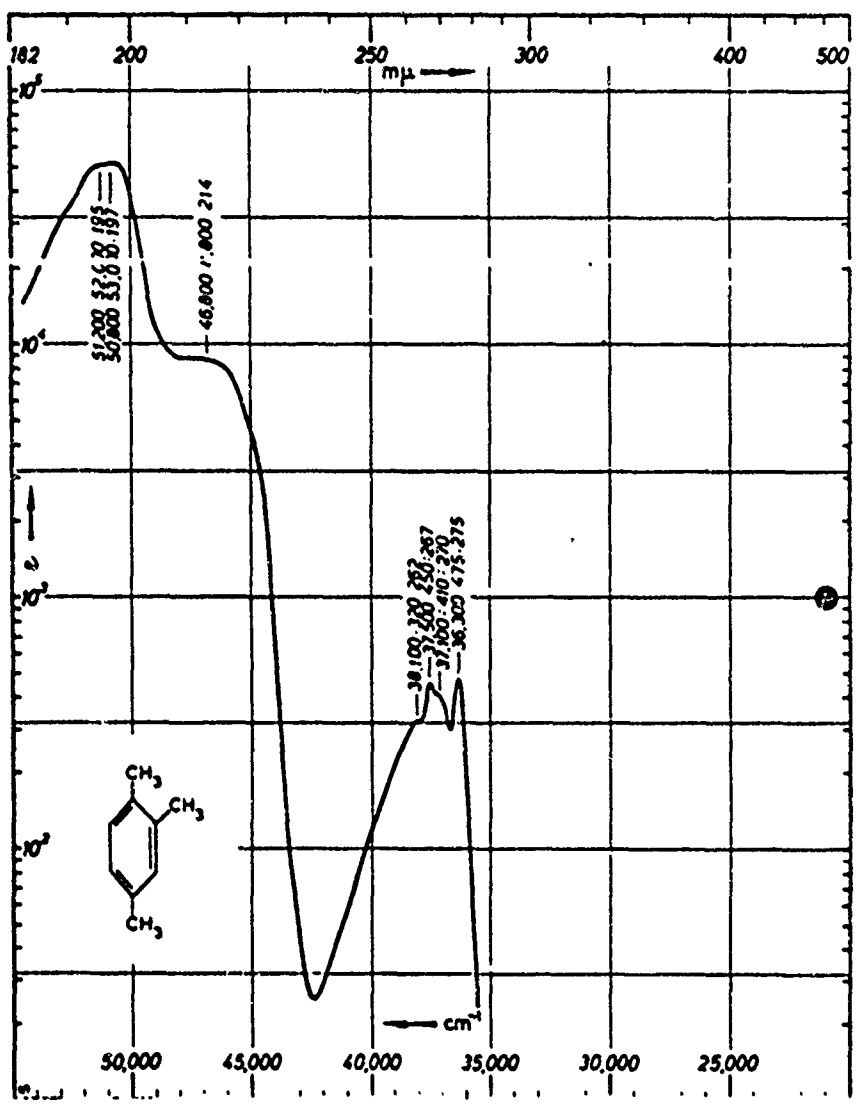


Figure 8. UV Spectrum of 1,2,4-Trimethylbenzene in Hexane (From UV Atlas of Organic Compounds, Plenum Press, N.Y.)

Naphthalene Naphthalin		E 1/1 32 000/00 600
Spectrometer Spektrometer Cary 1", Hilger Uvispek	Solvent Lösungsmittel Hexane	Formula Formel $C_{10}H_8$
Spec. resn Spek. Auflösung 30 cm^{-1} at 45,200 cm^{-1} 12 cm^{-1} at 36,400 cm^{-1} 11 cm^{-1} at 33,300 cm^{-1}	Concn Konz. $5{\cdot}896 \times 10^{-5}$, $1{\cdot}179 \times 10^{-4}$, $2\,220 \times 10^{-4}$, $2{\cdot}948 \times 10^{-4}$, $5\,551 \times 10^{-4}$, $1\,112 \times 10^{-3}$, $5{\cdot}56 \times 10^{-3}$, $1{\cdot}112 \times 10^{-2}$ M	Mol. wt Mol. Gew 128·2 m.p. 80·2°
Cell length Schichtdicke 0·526, 2·0, 5·0 cm	Purity Reinheit Zone refined	I.R ·9021, 9238
E. M. F. Roe: Chester Beatty Res. Inst., Royal Cancer Hospital, London		

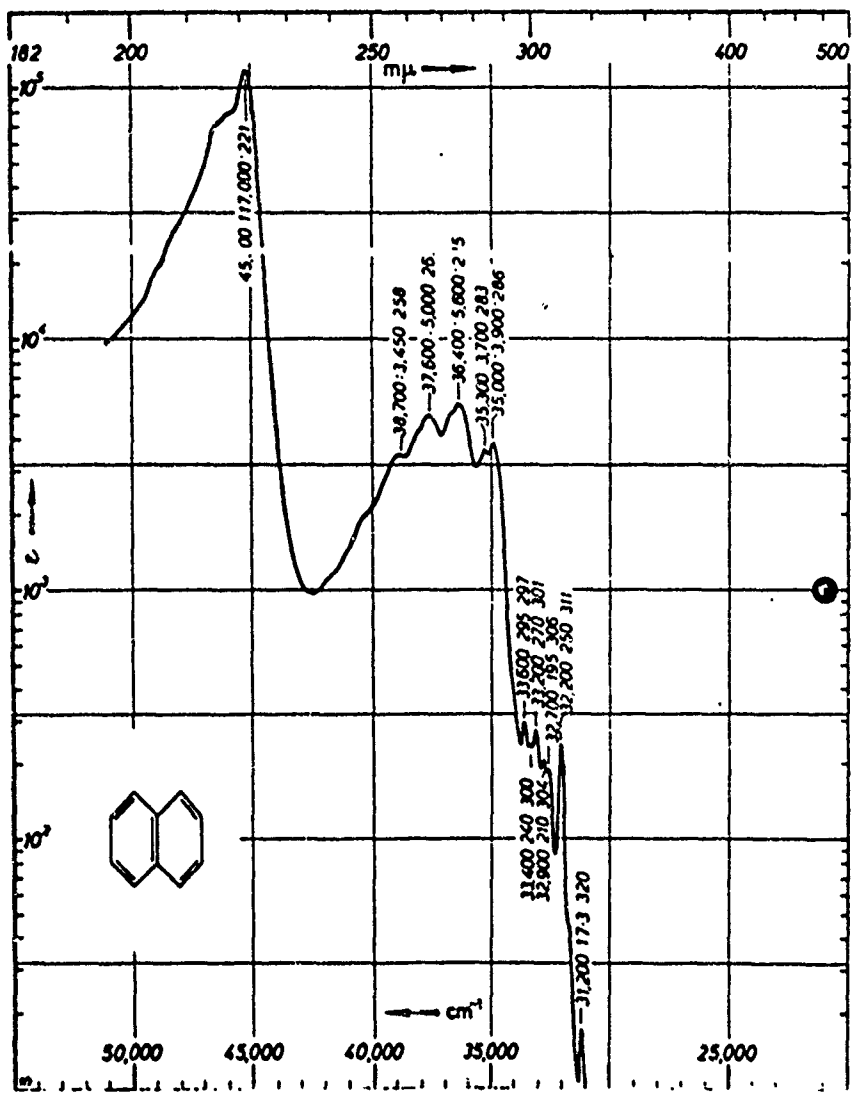


Figure 9. UV Spectrum of Naphthalene in Hexane (From UV Atlas of Organic Compounds, Plenum Press, N.Y.)

TABLE 3. GC-UVD RESPONSE OF REFERENCE COMPOUNDS AT VARIOUS WAVELENGTHS

Compound	Concentration µg/ml	Retention Time, Minutes	Relative Response[a] at Given Wavelength, nm													
			208	212	216	220	224	228	232	236	240	244	248	252	256	260
1. Benzene	500	1.43	0.2	0.1	--	--	--	--	--	--	--	--	--	--	--	--
2. Toluene	500	2.03	0.9	0.7	0.3	0.1	--	--	--	--	--	--	--	--	--	--
3. Ethylbenzene	500	3.11	0.7	0.4	0.3	0.1	--	--	--	--	--	--	--	--	--	--
4. p-Xylene	500	3.28	1.0	1.1	0.9	0.7	0.3	0.1	--	--	--	--	--	--	--	--
5. o-Xylene	500	3.63	1.0	0.9	0.5	0.2	0.1	--	--	--	--	--	--	--	--	--
6. n-Propylbenzene	500	4.86	0.8	0.7	0.4	0.1	--	--	--	--	--	--	--	--	--	--
7. 1-Ethyl-4-methylbenzene	500	5.10	0.8	0.8	1.1	0.8	0.1	0.1	--	--	--	--	--	--	--	0.1
8. 1,3,5-Trimethylbenzene	500	5.25	1.5	1.6	1.3	1.2	0.7	0.3	0.1	--	--	--	--	--	--	0.1
9. 1,2,4-Trimethylbenzene	500	5.85	1.0	1.2	0.9	0.7	0.5	0.2	0.1	--	--	--	--	--	--	--
10. Indane	500	6.85	1.1	1.0	0.6	0.3	0.1	--	--	--	--	--	--	0.1	0.1	0.2
11. 1,2,4,5-Tetramethylbenzene	580	9.60	1.5	1.3	1.1	0.8	0.3	0.3	0.2	0.1	--	--	--	--	--	0.1
12. Naphthalene	80	11.35	12.9	17.4	5.9	1.7	0.9	0.3	0.2	0.2	0.3	0.4	0.5	0.6	0.9	0.9
13. 2-Methylnaphthalene	67	15.20	8.8	12.2	13.9	4.5	1.8	1.0	0.4	0.3	0.2	0.4	0.4	0.5	0.8	0.7
14. Biphenyl	505	18.25	2.1	1.2	0.9	1.0	1.3	1.7	2.0	2.2	2.4	2.2	2.1	1.8	1.3	1.0
15. 2-Ethylnaphthalene	500	18.80	7.1	8.8	11.8	5.4	2.1	1.3	0.6	0.4	0.4	0.4	0.5	0.7	0.7	0.8
16. 2,6-Dimethylnaphthalene	62	19.15	11.6	20.8	24.6	14.8	4.8	1.9	1.4	0.8	1.0	1.2	1.3	1.5	1.2	1.1
17. 2,3-Dimethylnaphthalene	55	20.20	7.6	12.5	14.7	8.6	3.0	1.3	0.9	0.5	0.3	0.3	0.4	0.6	0.7	0.9
18. 1,2-Dimethylnaphthalene	58	20.65	4.3	5.7	8.2	6.8	2.5	0.8	0.5	0.3	--	--	--	--	0.3	0.5
19. 2,3,6-Trimethylnaphthalene	63	21.85	22.1	14.6	10.2	7.3	6.9	8.7	10.6	12.7	14.1	13.6	13.4	11.7	9.1	7.5
20. 3-Methylbiphenyl	510	23.95	0.6	0.9	1.3	1.4	0.8	0.3	0.1	0.1	--	--	--	--	--	0.1
21. 4,4'-Dimethylbiphenyl	505	25.90	2.9	1.6	1.0	0.8	0.9	1.2	1.5	1.9	2.2	2.2	2.5	2.5	2.2	2.0
22. Phenanthrene	545	30.55	3.2	2.4	2.3	1.8	2.1	3.4	4.7	7.1	7.9	7.8	3.7	2.7	2.1	1.8

a. Peak area response relative to that of 1,2,4-trimethylbenzene at 208 nm.

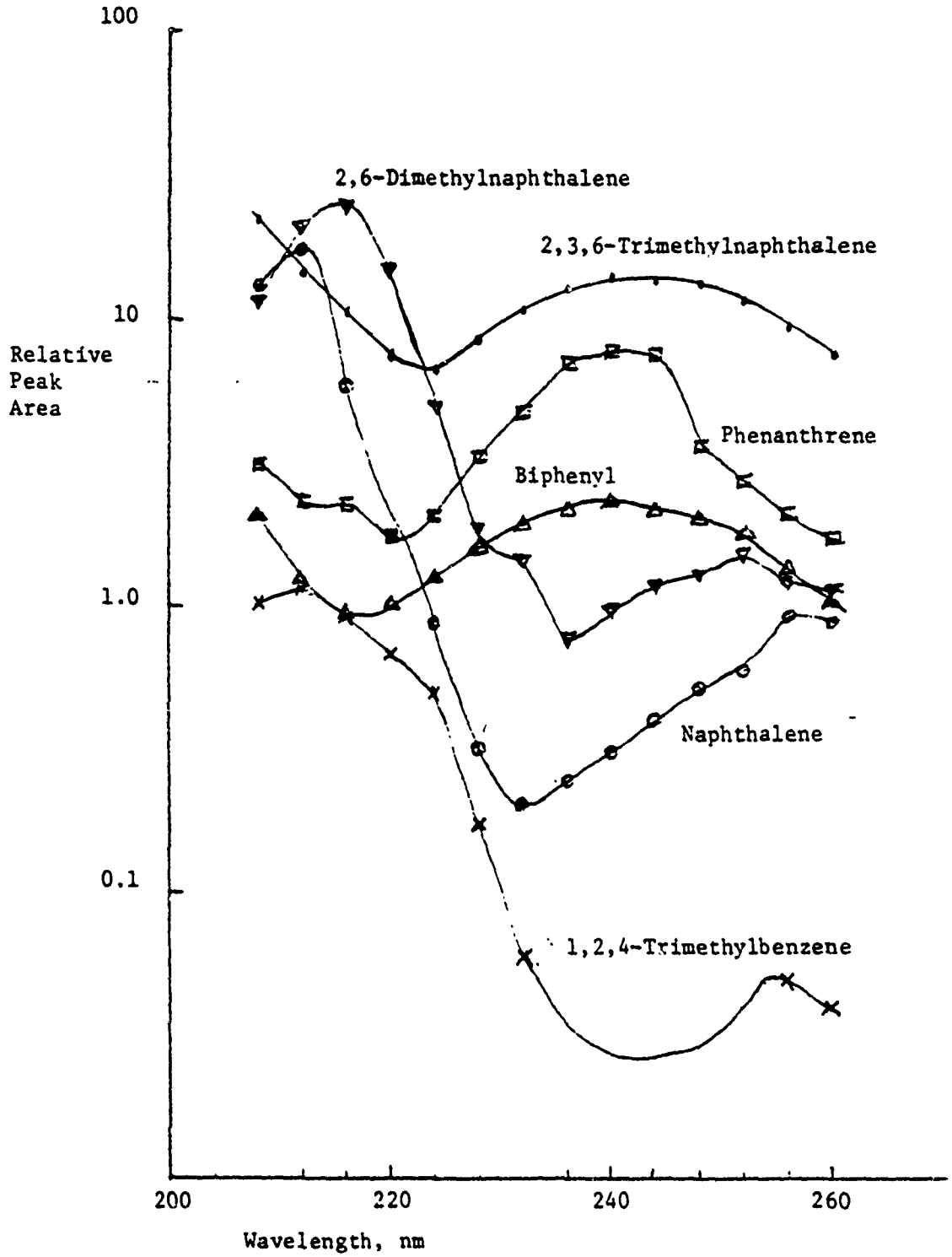


Figure 10. GC-UVD Response of Reference Compounds Versus Wavelength (Relative peak area is relative to that of 1,2,4-trimethylbenzene at 208 nm).

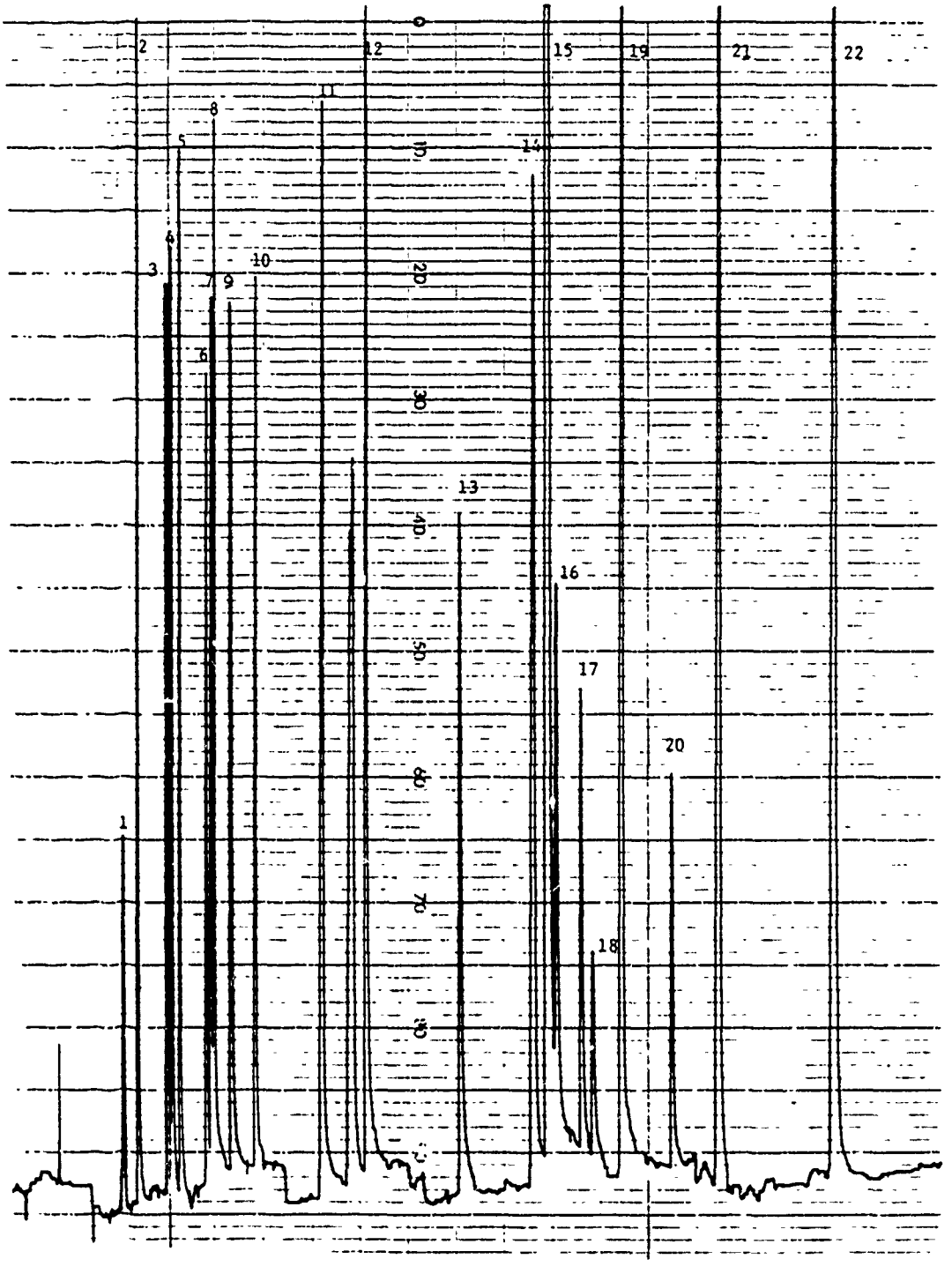


Figure 11. Gas Chromatogram of a Standard Mixture of Aromatic Hydrocarbons Using a UVD at 208 nm. (See Table 3 for identification of numbered peaks).

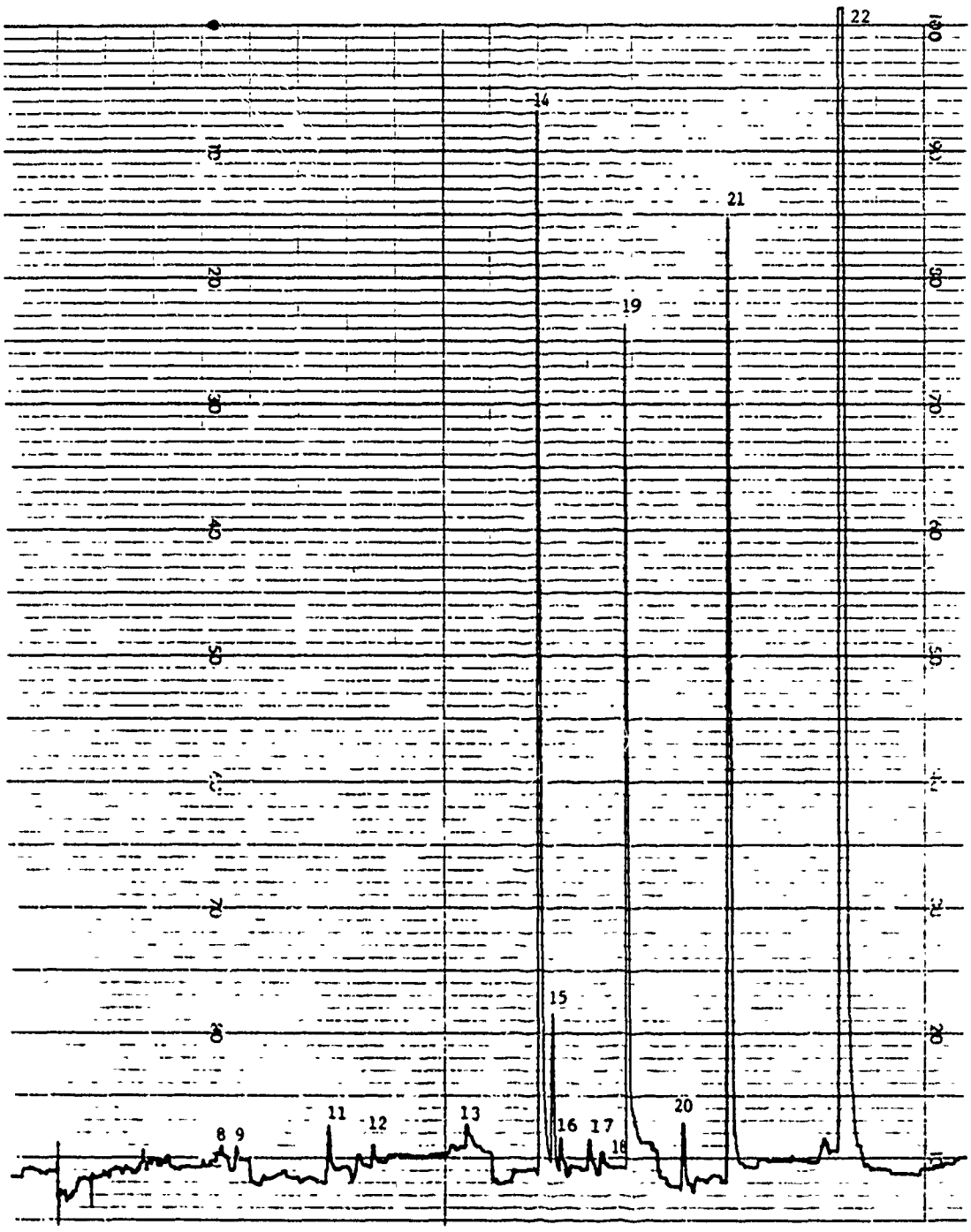


Figure 12. Gas Chromatogram of a Standard Mixture of Aromatic Hydrocarbons Using a UVD at 236 nm. (See Table 3 for identification of numbered peaks).

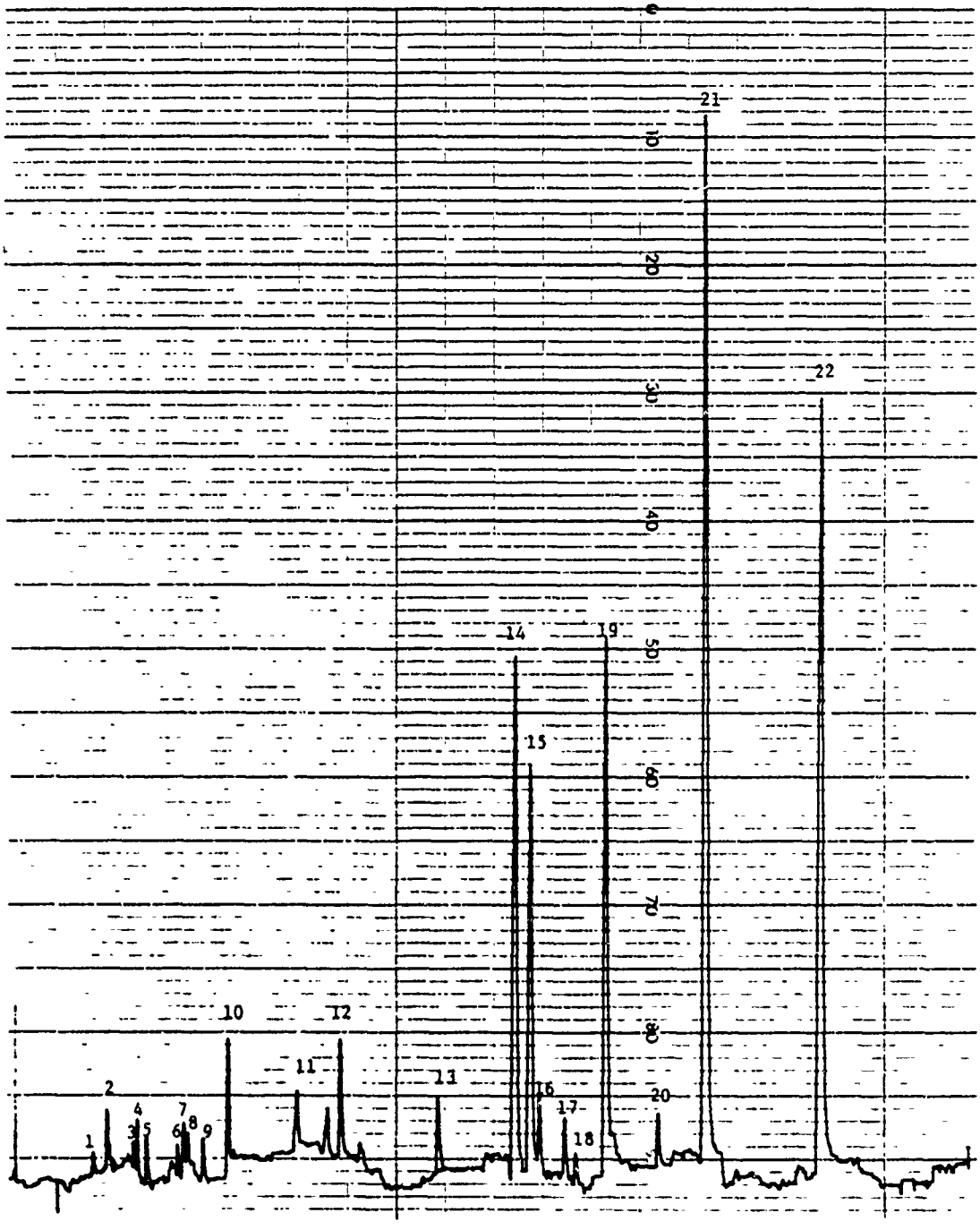


Figure 13. Gas Chromatogram of a Standard Mixture of Aromatic Hydrocarbons Using a UVD at 260 nm. (See Table 3 for identification of numbered peaks)

5. Response Versus Concentration

The response characteristics of five aromatic hydrocarbon reference compounds, namely toluene, o-xylene, 1,2,4-trimethylbenzene (pseudocumene), 1,2,4,5-tetramethylbenzene (durene), and naphthalene, were studied using the same conditions as described for the response versus wavelength studies. The compounds were dissolved in petroleum ether in concentrations ranging from 0.001wt % to 1.0 wt %. The lower concentration was dictated by the detection limit achievable and the upper limit was dictated by the capacity of the GC capillary column.

The response obtained was found to be linear in all cases as indicated by a slope of 1.0 for the log-log plots of response versus concentration. Representative plots, those for o-xylene and naphthalene, are given in Figures 14 and 15.

Data obtained from the analysis of neat fuels, described on page 40, has shown that the detector can become saturated at very high levels. The linear range of the detector is approximately 10^3.

6. Precision

The precision of retention times and detector response was determined using ten different reference compounds, six benzenes and four naphthalenes. The detector response was measured as the response factor relative to an internal standard, p-fluorotoluene, using peak height data. Because of the complexity of most fuel samples, many of the GC peaks have shoulders caused by the presence of unresolved minor components. Consequently quantification based on peak heights is considered more reliable than that based on area measurements.

Six different calibration solutions prepared in hexane were studied covering the range of 10 to 450 µg/ml for the benzenes and 1 to 45 µg/ml for the naphthalenes. A narrow-bore (0.25 mm) SE-30 fused silica capillary column was used with a 2 µl injection and a 10:1 split. Four to eight replicates were analyzed at each concentration level which represented a

total of 32 runs. The response factor data obtained are given in Table 4. The precision data are summarized in Table 5 along with the average retention times and response factors for the 32 runs.

The retention times were highly reproducible, generally to within a few seconds, and gave relative standard deviations of a few tenths of a percent in most cases. The response factors gave relative standard deviations of 1 to 20 percent at the different levels with the higher values occurring at the lower concentration levels. The relative standard deviation of the weighted average response factors over the entire concentration range varied from 5.8 to 17.1 percent which indicated some degree of linearity but less than desired. A portion of the variation may have been caused by variations in the injector discrimination at various concentration levels rather than by variations in the detector response. The use of an on-column injector for capillary work would be required to eliminate injector discrimination.

Precision data at a single concentration level, 2.0 wt % for benzenes and 0.2 wt % for naphthalenes, were also obtained using a calibration solution prepared in a nonaromatic fuel (Garrett Jet A, from Exxon Program, 1976). For these analyses a wide-bore (0.32 mm) SE-30 fused silica capillary column was used with a 1-µl injection and a 100:1 split. The retention time and response factor data obtained are given in Table 6 along with data obtained at a comparable concentration level using a calibration solution prepared in hexane. The retention time precision ranged from 0.1 to 0.7% and the response factor precision ranged from 1 to 10%. In general the precision obtained using hexane solutions was better than that obtained using a neat fuel. The higher split ratio required for the injection of a neat fuel very likely had an adverse affect upon the precision.

7. UVD/FID Studies

The nondestructive nature of the UVD permits other detectors to be used satisfactorily in series with it. As described in the section on instrument modifications on page 17, the exit end of the UV detector cell was connected in series with a flame ionization detector via a heated fused silica capillary transfer line. Makeup gas for the FID was introduced con-

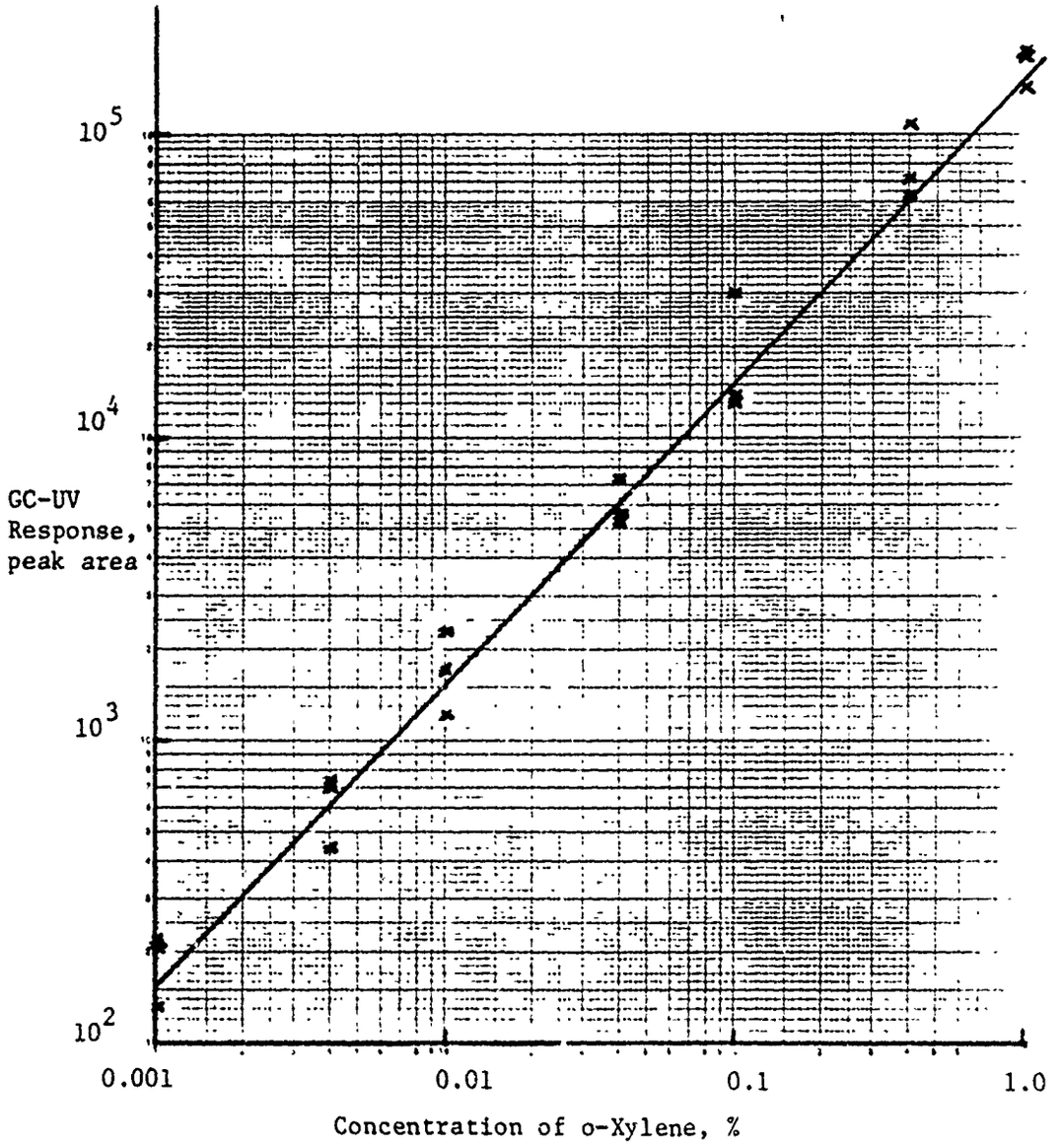


Figure 14. GC-UVD Response of o-Xylene Versus Concentration.

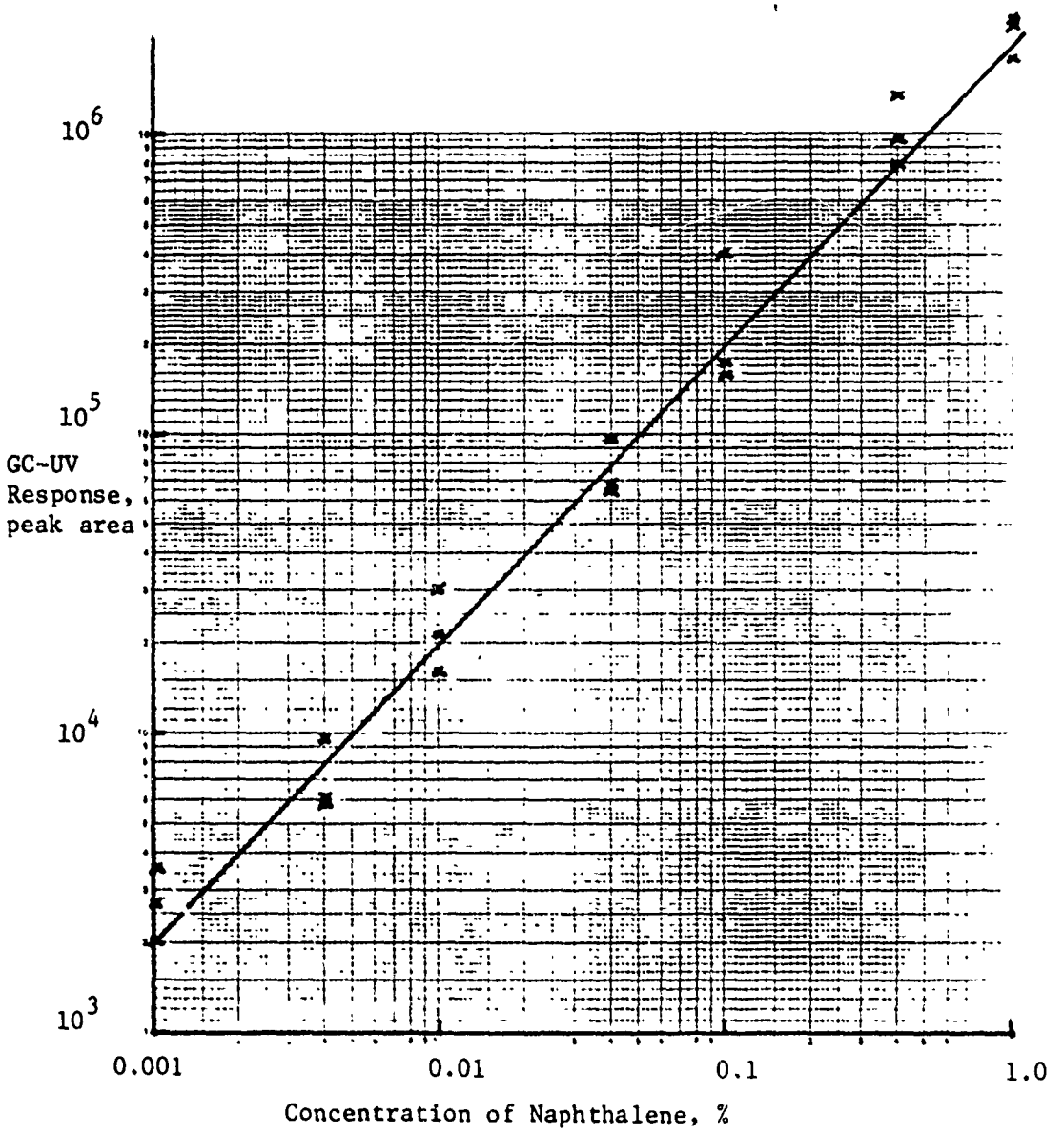


Figure 15. GC-UVD Response of Naphthalene Versus Concentration

TABLE 4. GC-UVD RESPONSE OF REFERENCE AROMATIC HYDROCARBONS AT VARIOUS CONCENTRATIONS

Compound	Response Factor[a] at Given Concentration, µg/ml						
	450	200	100	50	20	10	Average
Toluene	1.45	1.56	1.62	1.71	1.78	1.76	1.64
p-Xylene	1.24	1.32	1.35	1.41	1.36	1.30	1.33
o-Xylene	1.40	1.53	1.56	1.66	1.55	1.51	1.53
1-Ethyl-4-methylbenzene	0.93	0.97	0.98	1.04	0.90	0.99	0.97
1,2,4-Trimethylbenzene	1.14	1.21	1.23	1.28	1.24	1.15	1.21
1,2,4,5-Tetramethylbenzene	1.34	1.45	1.47	1.56	1.50	1.52	1.47
Naphthalene[b]	9.09	9.01	8.70	8.77	7.04	8.13	8.40
2-Methylnaphthalene[b]	6.33	5.99	5.49	5.49	4.67	ND[c]	5.52
2,3-Dimethylnaphthalene[b]	5.18	4.98	4.65	4.52	4.00	5.92	4.81
2,3,6-Trimethylnaphthalene[b]	3.79	3.65	2.38	3.56	3.13	4.74	3.62

(a) Average of four runs each at the 10, 50 and 450-µg/ml levels, six runs each at the 20 and 100 µg/ml levels, and eight runs at the 200 µg/ml level. The response factors (RF) are based on peak heights relative to the peak height of p-fluorotoluene used as an internal standard at a concentration of 250 µg/ml in all runs.

$$RF = \frac{\text{Pk. Ht. of Cpd.}}{\text{Pk. Ht. of p-FT}} \times \frac{250}{\text{Concn. of Cpd.}}$$

(b) The concentration of naphthalenes was one tenth of the given level, i.e. 45, 20, 10, 5, 2, and 1 µg/ml.

(c) Not detected.

TABLE 5. SUMMARY OF GC-UVD RESPONSE DATA

Compound	Retention Time		Response Factor[c]	
	Avg., min[a]	% RSD[b]	Avg.[a]	% RSD
Toluene	4.62	0.4	1.65	8.6
p-Xylene	7.44	0.4	1.33	5.8
o-Xylene	8.15	1.7	1.53	6.5
1-Ethyl-4-methylbenzene	10.86	0.5	0.98	7.7
1,2,4-Trimethylbenzene	12.08	0.3	1.21	7.6
1,2,4,5-Tetramethylbenzene	17.22	0.2	1.47	5.6
Naphthalene	19.41	0.2	8.46	11.4
2-Methylnaphthalene	23.95	0.2	5.59	11.3
2,3-Dimethylnaphthalene	29.43	0.1	4.88	13.6
2,3,6-Trimethylnaphthalene	33.40	0.1	3.69	17.1

(a) Weighted average of data from 32 runs. For the benzenes, the runs included four runs each at the 10, 50, and 450-µg/ml levels, six runs each at the 20 and 100-µg/ml levels, and eight runs at the 200 µg/ml level. The number of runs was the same for the naphthalenes as for the benzenes but the concentrations were lower by a factor of 10.

(b) Percent relative standard deviation.

(c) Response factor based on peak height relative to the peak height of p-fluorotoluene used as an internal standard at a concentration of 250 µg/ml.

$$RF = \frac{\text{Pk. Ht. of Cpd.}}{\text{Pk. Ht. of p-FT}} \times \frac{250}{\text{Concn. of Cpd.}}$$

TABLE 6. GC-UVD RESPONSE DATA FROM STANDARDS PREPARED IN HEXANE AND A NEAT FUEL

Compound	Retention Time		Response Factor	
	Avg., min.	% RSD	Avg. min.	% RSD
	Calibration Solution in Hexane[a]			
Toluene	4.61	0.70	1.56	0.6
p-Xylene	7.44	0.23	1.32	1.7
o-Xylene	8.14	0.25	1.53	1.7
1-Ethyl-4-methylbenzene	10.87	0.26	0.97	1.9
1,2,4-Trimethylbenzene	12.08	0.25	1.21	1.7
1,2,4,5-Tetramethylbenzene	17.22	0.18	1.45	2.0
Naphthalene	19.40	0.17	9.01	1.8
2-Methylnaphthalene	23.93	0.12	5.99	2.3
2,3-Dimethylnaphthalene	29.41	0.10	4.98	2.8
2,3,6-Trimethylnaphthalene	33.39	0.07	3.65	10.5
	Calibration Solution in Nonaromatic Fuel[b]			
Benzene	2.72	0.58	0.41	1.8
Toluene	4.13	0.66	1.23	0.5
p-Xylene	6.60	0.74	1.14	4.2
o-Xylene	7.21	0.58	1.24	2.3
1,2,3,4-Tetramethylbenzene	15.57	0.46	1.06	2.4
Naphthalene	17.52	0.33	8.13	4.5
2-Methylnaphthalene	21.85	0.24	5.99	8.0
2,3-Dimethylnaphthalene	27.04	0.12	7.25	4.3

(a) Benzenes and naphthalenes were present at concentrations of 200 and 20 µg/ml, respectively; when used for the calibration of 1% solutions of fuel in hexane, these concentrations correspond to 2.0 wt % and 0.2 wt %, respectively, in the fuel.

(b) Benzenes and naphthalenes were present at concentrations of 2.0 wt % and 0.2 wt % respectively.

centrically around the exit end of the transfer line and eliminated any dead volume at the connection. Peak width measurements showed that there was no detectable loss of chromatographic performance between the UVD and the FID.

When the FID was used in series with the UVD for the GC analysis of hexane solutions of fuels, many of the lower-boiling components could not be detected by the FID because of interference from the solvent peak. However, when injection of a neat fuel was used, all major components could be readily detected by the FID. GC-FID chromatograms are shown in Figures 16 to 19 along with the GC-UVD chromatograms obtained simultaneously during analysis of several representative fuel samples.

8. Analysis of Aircraft Fuels

Twenty fuel samples submitted by WPAFB were analyzed by GC-UVD, using the system described above, to determine the amounts of the major individual aromatic hydrocarbons present. A description of the samples is given in Table 7. The fuels were diluted with n-hexane and spiked with p-fluorotoluene as an internal standard to give solutions containing 10 mg of fuel and 250 µg of p-fluorotoluene per ml. The internal standard level in the fuel was therefore 250 µg/10 mg or 2.5 g/100g. Phenanthrene was added as a performance standard at a level of 200 µg/ml. The following GC conditions were used:

Gas Chromatograph	--	Varian Model 2740
Automatic injector	--	Hewlett Packard Model 7670A
Sample volume	--	2 µl, 10:1 split
Injector temperature	--	200°C
Transfer line temperature	--	200°C
Detector temperature	--	200°C
Column	--	30-m x 0.25-mm SE-30 fused silica
Column temperature	--	programmed from 30°C to 200°C at 4°C/minute
Carrier gas	--	hydrogen at 50 cm/sec
Detector wavelength	--	208 nm
Data system	--	Computer Inquiry Systems CIS-CALS

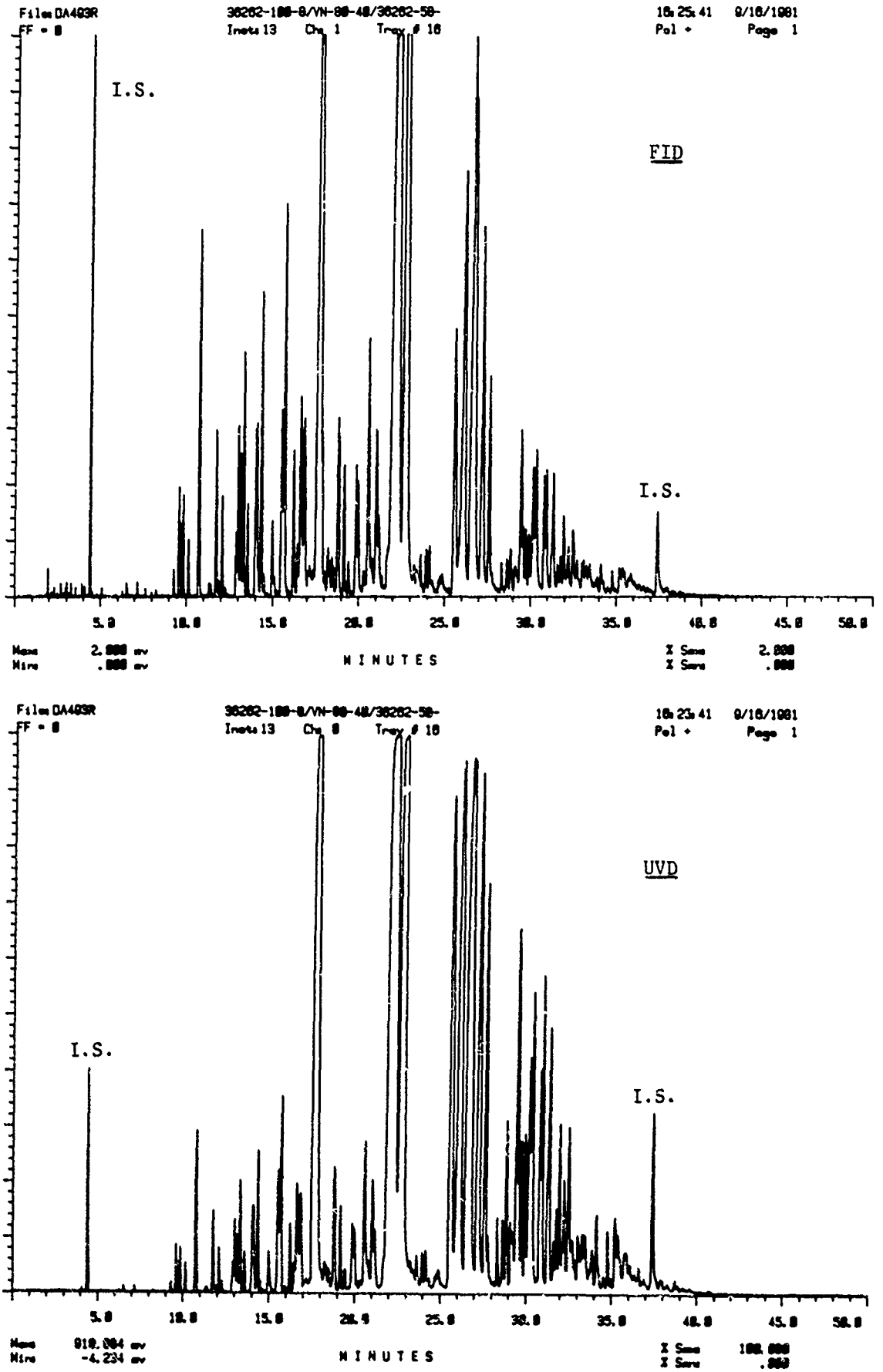
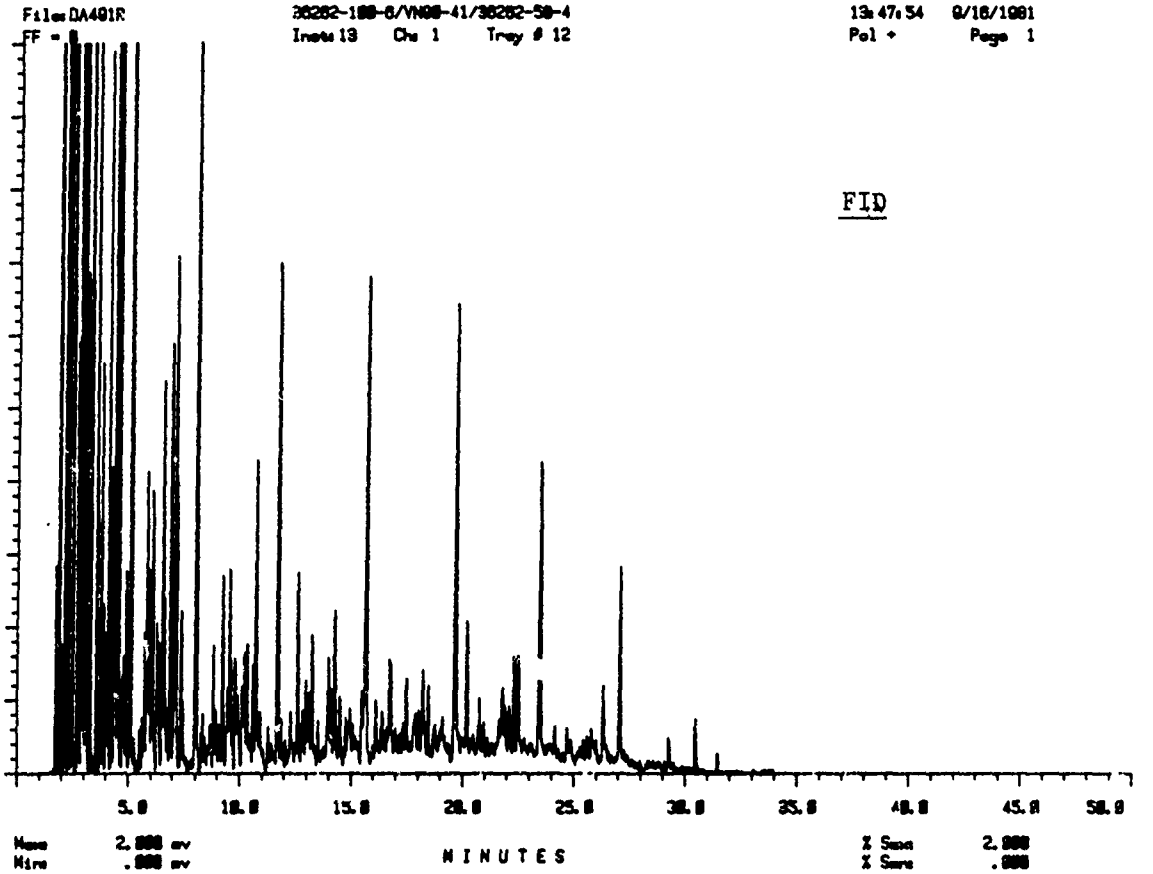


Figure 16. GC-FID and GC-UVD Chromatograms Obtained Simultaneously From Analysis of Fuel Sample VN-80-40.



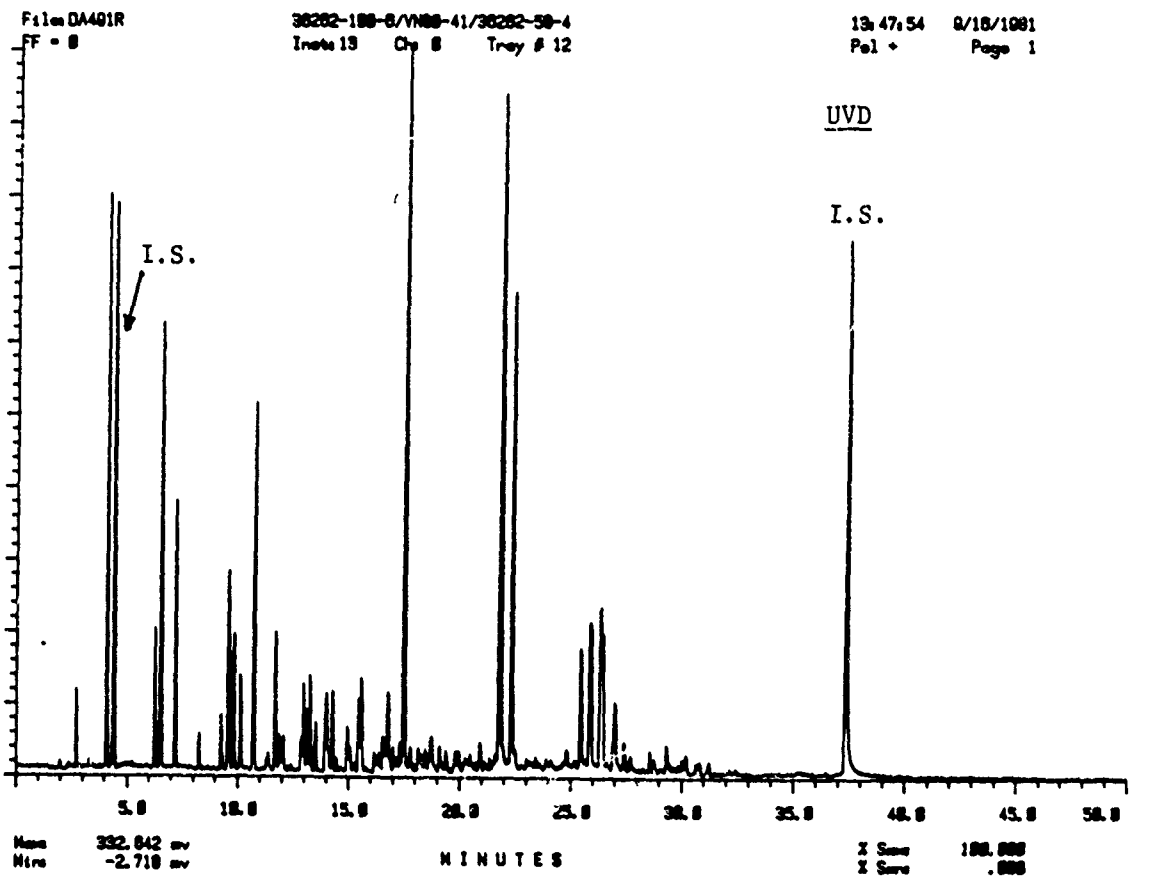


Figure 17. GC-FID and GC-UVD Chromatograms Obtained Simultaneously From Analysis of Fuel Sample VN-80-41.

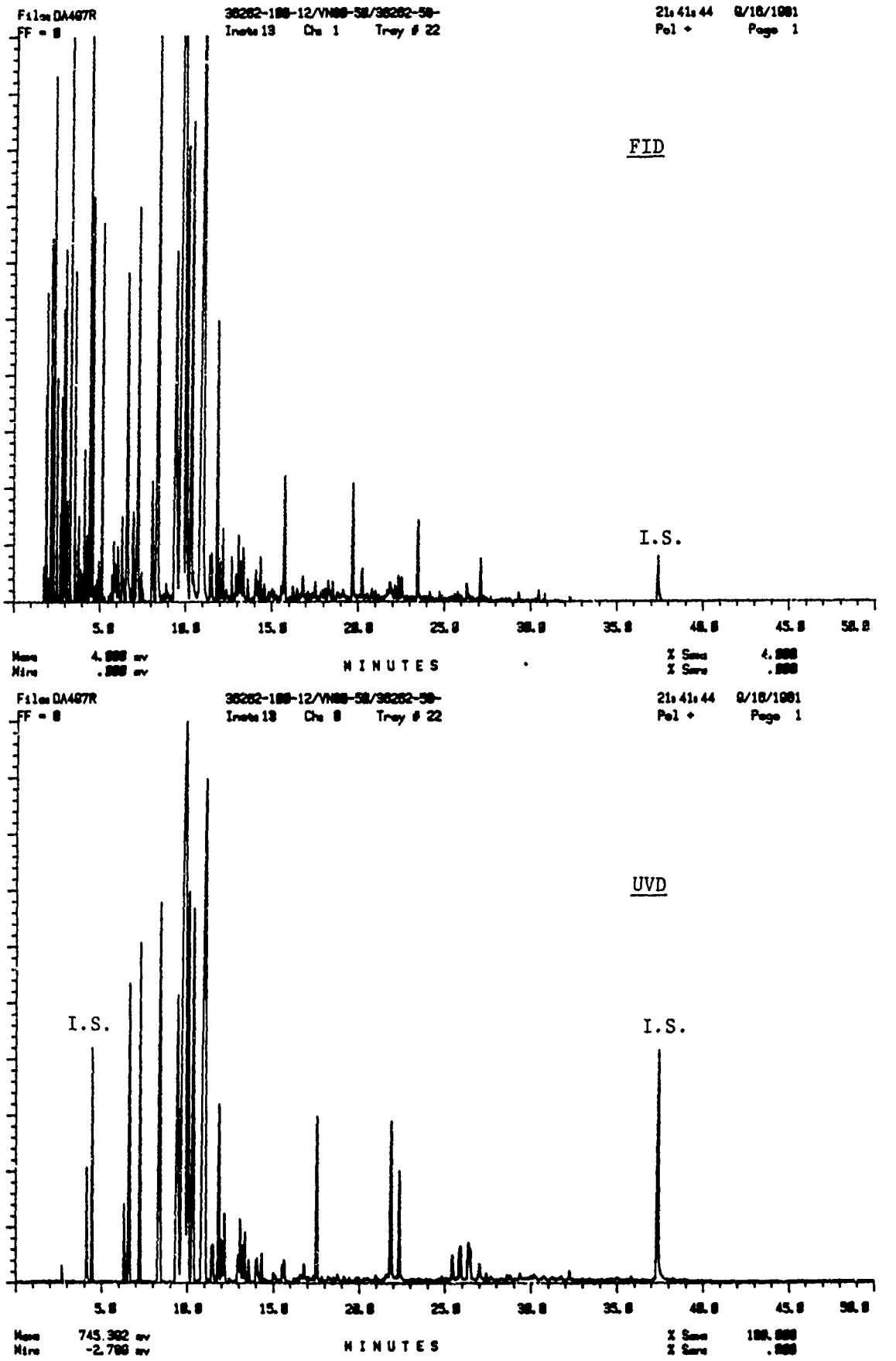


Figure 18. GC-FID and GC-UVD Chromatograms Obtained Simultaneously From Analysis of Fuel Sample VN-80-50.

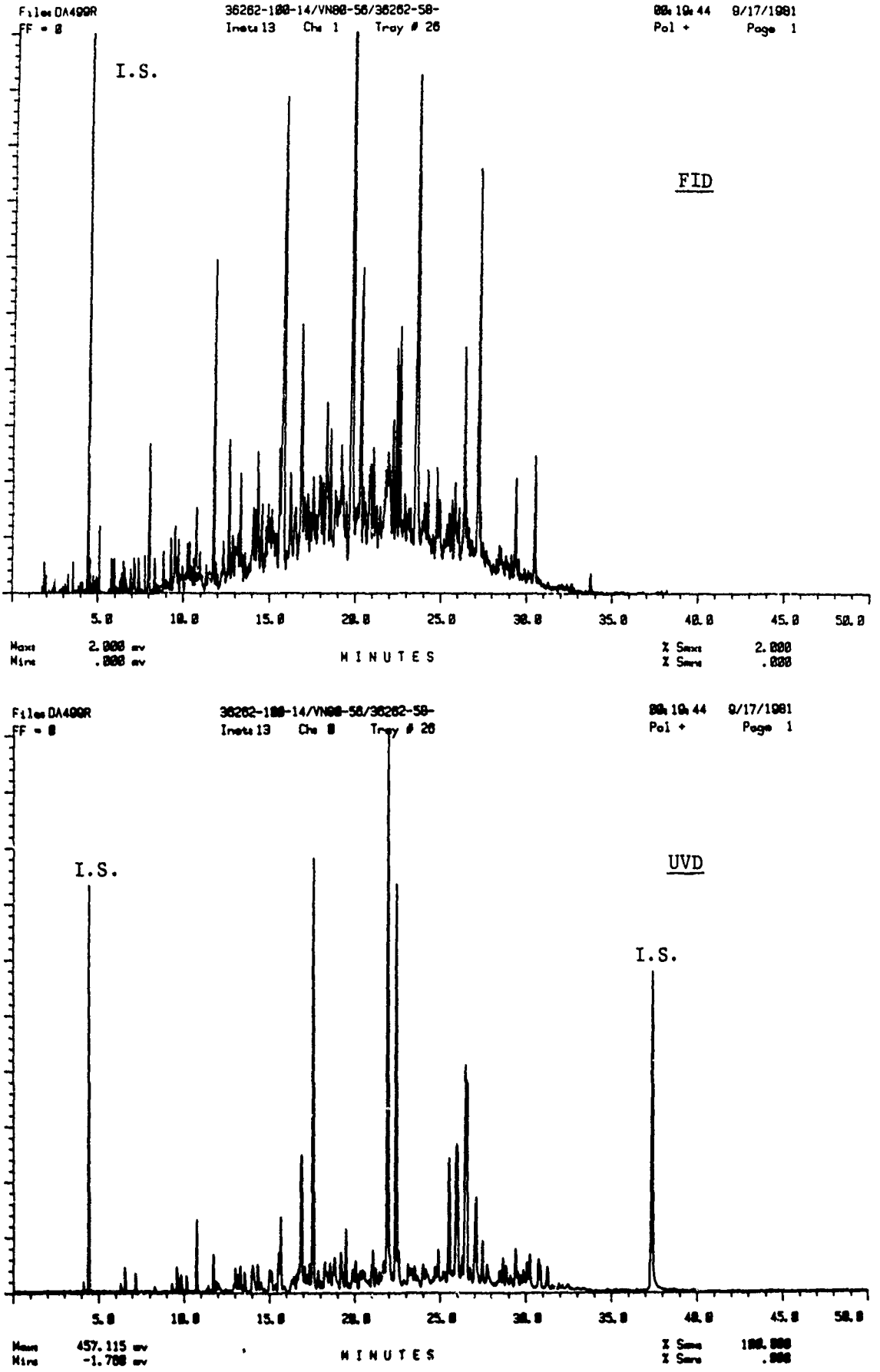


Figure 19. GC-FID and GC-UVD Chromatograms Obtained Simultaneously From Analysis of Fuel Sample VN-80-56.

TABLE 7. FUEL SAMPLES SUPPLIED TO BATTELLE BY AFWAL/POSF

Sample No.	Description
VN-80-39	Xylene Bottoms (Alkylbenzenes)
VN-80-40	2040 Solvent (Alkylnaphthalenes)
VN-80-41	JP-4 Fuel 1A
VN-80-47	JP-8 - 2040 Solvent Blend
VN-80-48	JP-4 - 2040 Solvent Blend
VN-80-50	JP-4 - Xylene Bottoms Blend
VN-80-52	JP-4 - Xylene Bottoms - GMSO* Blend
VN-80-56	JP-8 Fuel 2B
VN-80-59	Diesel Fuel
VN-80-60	Diesel - 2040 Solvent Blend
VN-80-61	Shale JP-4 Fuel 15B
VN-80-62	Shale JP-8
VN-80-67	Shale JP-4 (HRI)
VN-80-68	JP-4 (P&W)
VN-80-69	JP-5 (GE T-13)
VN-80-70	JP-5 (F-1)
VN-80-71	ERBS Blending Stock
VN-80-72	ERBS Fuel 3B
VN-80-73	ERBS Blend (3B-11.8)
VN-80-74	ERBS Blend (3B-12.3)

* GMSO - Gulf Mineral Seal Oil.

All analyses were performed in triplicate. A standard solution was analyzed after each five samples. The data obtained were included in the precision data presented above. The estimated detection limits for benzenes and naphthalenes were 10 µg/ml of solution and 2 µg/ml, respectively. Since the solutions contained 1 wt % of fuel in hexane, these detection limits correspond to 0.1 wt % and 0.02 wt % in the fuel, respectively.

A total of 57 components were quantified in the various fuels. The tentative identification of the components was based upon the GC pattern and the data obtained from the GC-MS analysis of aromatic fractions separated by adsorption column chromatography. The identifying numbers assigned to the components are the same as those reported in Table 2. A listing of the 57 components and the response factors used for their quantification is given in Table 8.

The aromatic hydrocarbon composition of the 20 fuel samples, reported as four sets of five samples each, are presented in Tables C1 to C4 in Appendix C. The standard deviations calculated from the triplicate data are included. Representative chromatograms for each of the 20 fuel samples are given in Figures C-1 to C-20 in Appendix C.

Eight of the above fuel samples were also analyzed by GC-UVD by injection of the neat fuels. For these analyses a wide-bore SE-30 fused silica column was used, 0.32 mm I.D. instead of 0.25 mm I.D. An injector temperature of 250°C and a 1-µl injection with a 100:1 split was used. All other GC operating conditions were the same as those listed above.

p-Fluorotoluene was added to each fuel sample as an internal standard at a level of 2.0 wt %. Phenanthrene was added as a reference compound at a level of 0.7 wt %. Three replicate analyses were performed with each sample. A standard mixture was analyzed after every fifth sample. The standard mixture contained five benzenes at a level of 2.0 wt % and three naphthalenes at a level 0.2 wt % in a nonaromatic fuel. The data obtained from the standard were included in the precision data presented above. The response factors obtained from the standard and used for the quantifications are included in Table 8. The estimated detection limits for benzenes and naphthalenes in the fuels were 0.01 wt % and 0.002 wt %, respectively. These detection limits were ten-fold lower than those obtained

TABLE 8. RESPONSE FACTORS USED FOR QUANTIFICATION OF AROMATIC HYDROCARBONS DETERMINED IN AIRCRAFT FUELS BY GC-UVD

GC Peak No.[a]	Tentative Identification[b]	Response Factor[c] Used for Quantification in GC-UVD Analysis Using Given Solvent	
		Hexane	Nonaromatic Fuel
0	Benzene	(d)	0.41
1	Toluene	1.64	1.23
2	Ethylbenzene	1.64	1.23
3	m & p-Xylene	1.64	1.14
4	o-Xylene	1.64	1.24
5	Isopropylbenzene	1.64	1.24
6	Propylbenzene	1.64	1.24
7	1-Ethyl-4-methylbenzene	1.00	1.24
8	1,3,5-Trimethylbenzene	1.00	1.24
9	1-Ethyl-2-methylbenzene	1.33	1.24
10	1,2,4-Trimethylbenzene	1.33	1.24
13	1,2,3-Trimethylbenzene	1.54	1.24
15	1-Methyl-2-isopropylbenzene	1.54	1.24
16	Indane	1.54	1.24
17	1-Methyl-3-propylbenzene	1.54	1.24
18	1-Methyl-4-propylbenzene	1.22	1.24
19	1,3-Dimethyl-5-ethylbenzene	1.22	1.24
20	1-Methyl-2-propylbenzene	1.22	1.24
21	1,3-Dimethyl-2-ethylbenzene	1.22	1.24
22	1,3-Dimethyl-4-ethylbenzene	1.22	1.24
23	1,2-Dimethyl-4-ethylbenzene	1.22	1.24
24	C_5-Benzene	1.22	1.24
25	C_5-Benzene	1.22	1.24
27	1,2-Dimethyl-3-ethylbenzene	1.22	1.24
28	1,2,4,5-Tetramethylbenzene	1.47	1.06
29	Methylindane	1.47	1.06
31	C_5-Benzene	1.47	1.06
32	1,2,3,4-Tetramethylbenzene	1.47	1.06
33	C_5-Benzene	1.47	1.06
34	C_5-Benzene	1.47	1.06
39	Naphthalene	8.33	8.13
40	C_5-Benzene	8.33	1.06
42	C_5-Benzene	8.33	1.06
44	C_5-Benzene	8.33	1.06
47	C_5-Benzene	8.33	1.06
49	C_2-Indane	8.33	1.06
50	C_2-Indane	8.33	1.06
54	2-Methylnaphthalene	5.56	5.99
55	1-Methylnaphthalene	5.56	5.99
56	C_4-Benzene	5.56	5.99
62	2-Ethylnaphthalene	5.56	5.99
64	2,6-Dimethylnaphthalene	5.56	5.99
65	1,6-Dimethylnaphthalene	5.56	5.99
67	2,3-Dimethylnaphthalene	4.76	7.25
69	1,2-Dimethylnaphthalene	4.76	7.25
71	Methylbiphenyl	4.76	7.25
73	C_3-Naphthalene	4.76	7.25
77	C_3-Naphthalene	4.76	7.25
78	C_3-Naphthalene	4.76	7.25
79	C_3-Naphthalene	4.76	7.25
80	C_3-Naphthalene	4.76	7.25
81	C_3-Naphthalene	4.76	7.25
82	C_3-Naphthalene	4.55	7.25
84	C_2-Biphenyl	4.55	7.25
89	C_4-Naphthalene	4.55	7.25
90	C_4-Naphthalene	4.55	7.25
91	C_4-Naphthalene	4.55	7.25
92	C_4-Naphthalene	4.55	7.25

(a) Peak number assignments are those used in Figure 1 and Table 2.

(b) Based on GC-MS studies of aromatic fractions obtained by adsorption column chromatography.

(c) The response factors (RF) are based on peak height of the compound relative to the peak height of p-fluorotoluene used as an internal standard.

(d) Not quantified.

from the analysis of hexane solutions. The lower detection limits were possible because the wider-bore column permitted the injection of a larger sample amount and because a better shielding of the detector from stray light permitted greater detector stability to be achieved. In many cases, however, these lower detection limits could not be realized because of interference from numerous minor components in a fuel. In such cases the higher detection limits were reported.

The aromatic hydrocarbon composition of the eight fuel samples, reported as two sets of four samples each, are presented in Tables C-5 and C-6 in Appendix C. The standard deviations calculated from the triplicate data are included. Representative chromatograms for each of the 8 fuel samples are given in Figures C-21 to C-28 in Appendix C.

The data obtained from the analysis of neat fuels often agreed with that obtained from the analysis of hexane solutions and at other times differed by as much as a factor of two or more. A representative comparison, based on the data from VN-80-40, is given in Table 9. Part of the differences may result from injector discrimination and part may result from the use of different reference compounds for estimating response factors. In some cases the levels determined from the analysis of neat fuels were so high they were outside the linear range of the detector. The analytical precision was good for both methods; the relative standard deviation was generally less than 10% and frequently less than 5%. It is expected that reliable quantitative data can be achieved by either method if reference samples are obtained for each compound of interest and calibration curves are prepared over the entire concentration range of interest. The injected amount would need to be reduced if necessary to avoid detector saturation.

D. PHOTOIONIZATION DETECTOR STUDIES

A photoionization detector (PID), HNU Systems Model PI-52, which featured special seals for high temperature operation and low dead volume for

Peak No.[a]	Amount Found,[b] g/100 g, Using Given Method	
	Hexane Solution	Neat Fuel
6	0.08 ± 0.06	0.08 ± 0.01
7	0.36 ± 0.02	0.38 ± 0.01
8	0.34 ± 0.05	0.35 ± 0.01
9	0.23 ± 0.08	0.23 ± 0.01
10	1.35 ± 0.06	1.46 ± 0.04
13	0.54 ± 0.01	0.68 ± 0.01
16	0.25 ± 0.01	0.35 ± 0.01
17	0.55 ± 0.05	0.63 ± 0.01
18	0.43 ± 0.03	0.53 ± 0.01
19	0.85 ± 0.01	0.94 ± 0.03
20	0.23 ± 0.03	0.32 ± 0.01
21	0.77 ± 0.03	0.92 ± 0.03
22	1.08 ± 0.05	1.21 ± 0.04
25	0.30 ± 0.02	0.36 ± 0.02
27	1.32 ± 0.08	1.19 ± 0.01
28	1.57 ± 0.03	2.09 ± 0.07
29	0.39 ± 0.03	0.64 ± 0.02
30	0.80 ± 0.07	1.19 ± 0.04
32	0.72 ± 0.01	1.11 ± 0.04
39	3.93 ± 0.38	0.94 ± 0.03[c]
42	1.07 ± 0.03	1.39 ± 0.04
44	0.62 ± 0.02	0.90 ± 0.03
49	1.15 ± 0.05	1.63 ± 0.04
50	0.87 ± 0.02	1.22 ± 0.07
54	6.40 ± 0.68	1.29 ± 0.05[c]
55	5.31 ± 0.53	1.29 ± 0.05[c]
62	1.99 ± 0.12	1.10 ± 0.04
64	2.50 ± 0.16	1.20 ± 0.04
65	2.88 ± 0.21	1.21 ± 0.05
67	2.04 ± 0.19	0.92 ± 0.03
69	1.08 ± 0.06	0.67 ± 0.03
71	0.93 ± 0.03	0.26 ± 0.01
73	0.90 ± 0.07	0.60 ± 0.02
77	0.51 ± 0.02	0.39 ± 0.02
78	0.70 ± 0.03	0.51 ± 0.02
79	0.40 ± 0.02	[d]
80	0.64 ± 0.03	0.51 ± 0.02
81	0.48 ± 0.03	0.42 ± 0.02
82	0.32 ± 0.04	0.25 ± 0.01
84	0.35 ± 0.02	0.26 ± 0.02
90	0.13 ± 0.02	0.11 ± 0.01
91	0.09 ± 0.01	0.08 ± 0.01
92	0.16 ± 0.02	0.11 ± 0.01

(a) The tentative identifications of the GC peaks are given in Table 7.

(b) Average of three runs is given with the standard deviation.

(c) The detector was saturated; the correct value is therefore considerably higher.

(d) This peak was not quantified because the data system did not resolve it from Peak No. 80.

use with capillary columns, was evaluated in terms of sensitivity, selectivity, and linearity for the determination of aromatic hydrocarbons. The following GC conditions were used:

Gas chromatograph	--	Carlo Erba Model 2150
Sample volume	--	2 µl, splitless
Injector temperature	--	200°C
Detector temperature	--	250°C
Column	--	30 m x 0.25 mm SE-52 Pyrex
Column temperature	--	50°C for 5 min., programmed to 230°C at 3°C/min.
Carrier gas	--	hydrogen at 50 cm/sec.
Make-up gas	--	helium at 20 ml/min.

Standard solutions containing three saturated hydrocarbons and three aromatic hydrocarbons were analyzed using both a 10.2-e.v. source and a 9.5-e.v. source. The relative response data obtained indicating the selectivity of the detector are given in Table 10. When the 10.2-e.v. source was used, a cyclic saturated hydrocarbon, cyclohexylcylohexane, gave approximately the same response as the aromatic hydrocarbons; i.e., there was no selectivity for aromatic hydrocarbons versus a cyclic saturated hydrocarbon. However, there was a 5 to 10-fold selectivity for aromatic hydrocarbons versus straight-chain saturated hydrocarbons. When a 9.5-e.v. source was used, the selectivity for aromatic hydrocarbons versus the cyclic saturated hydrocarbon was approximately 40 and the selectivity versus straight-chain saturated hydrocarbons was 100 to 200. The decrease in sensitivity for aromatic hydrocarbons using the 9.5-e.v. source instead of the 10.2-e.v. source was only about two. Therefore, it appears that the photoionization detector used with a 9.5-e.v. source may have some usefulness for the determination of aromatic hydrocarbons in jet fuels even though it does not provide the selectivity obtainable with an ultraviolet detector.

The PID with a 9.5-e.v. source was used to analyze standard solutions containing 0.1 to 50 µg/ml of the ten aromatic hydrocarbons used for the evaluation of the ultraviolet detector. The response data obtained are given in Table 11. The detector was found to be 10 to 100 times more sensitive than the ultraviolet detector; all of the compounds except toluene

TABLE 10. GC-PID SELECTIVITY FOR REFERENCE HYDROCARBONS

Compound	Relative Response[a] at 10.2 e.v.	Relative Response[a] at 9.5 e.v.	Response at 10.2 e.v. / Response at 9.5 e.v.
n-Octane	0.07	0.006	16.4
n-Dodecane	0.22	0.008	37.4
Cyclohexylcyclohexane	1.10	0.03	52.0
1,2,4,5-Tetramethylbenzene	1.00	1.00	1.4
Naphthalene	1.94	1.04	2.6
2-Methylnaphthalene	2.07	1.34	2.2

(a) Relative to the response obtained for an equal concentration of 1,2,4,5-tetramethylbenzene.

TABLE 11. GC-PID RESPONSE OF REFERENCE AROMATIC HYDROCARBONS

Compound	Relative Response[a] at Given Concn., µg/ml					
	0.1	0.5	2	10	50	Average ± S.D.
Toluene	ND[b]	0.08	0.05	0.05	0.09	0.07 ± 0.02
p-Xylene	0.36	0.38	0.42	0.43	0.49	0.42 ± 0.05
o-Xylene	0.12	0.09	0.07	0.10	0.14	0.10 ± 0.03
1-Ethyl-4-methylbenzene	0.46	0.54	0.53	0.54	0.60	0.53 ± 0.05
1,2,4,5-Tetramethylbenzene	1.44	1.15	1.21	1.28	1.30	1.28 ± 0.11
Naphthalene	0.80	0.66	0.74	0.83	0.96	0.80 ± 0.11
2-Methylnaphthalene	0.67	0.58	0.63	0.80	0.97	0.73 ± 0.16
2,3-Dimethylnaphthalene	0.54	0.47	0.53	0.74	0.96	0.65 ± 0.20
2,3,6-Trimethylnaphthalene	0.55	0.47	0.54	0.75	1.02	0.67 ± 0.22

(a) Peak area response relative to that of 1,2,4-trimethylbenzene presence at the same concentration.

(b) Not detected.

could be readily detected at 0.1 μg/ml. The response was not linear over the concentration range studied and the linearity varied considerably from compound to compound. The response per nanogram injected varied by as much as a factor of two over the concentration range studied. Also the relative responses varied considerably from compound to compound by as much as a factor of 15. The response variations of the photoionization detector are greater than those of the ultraviolet detector. In order to obtain reliable quantitative data from the use of a PID to determine aromatic hydrocarbons in fuel samples, a separate nonlinear calibration curve must be prepared for each compound of interest.

Several of the fuel samples were analyzed qualitatively using the glass capillary column GC-PID system described above fitted with the 9.5-e.v. source. Representative chromatograms are shown in Figures 20 and 21. There were no indications of saturated hydrocarbons being detected.

E. DETERMINATION OF NITROGEN-CONTAINING COMPOUNDS

Small amounts of nitrogen-containing compounds, especially pyrroles, reportedly can have very significant effects upon the performance of jet fuels. A portion of the project effort was, therefore, devoted to applying GC, GC-MS, and HPLC techniques to the determination of nitrogen-containing compounds in jet fuels.

1. GC Studies Using a Nitrogen-specific Detector

Crude shale oils, which serve as sources for some of the alternate jet fuels, generally contain very high concentrations of nitrogen-containing compounds. Most of these compounds are basic and are removed from the oil in subsequent processing. Nevertheless, small amounts of nitrogen-containing compounds may be carried through the processing and affect the performance of the fuels. A nitrogen-specific alkali-flame detector (AFD) was studied for the detection of the nitrogen-containing components.

The system used was a Varian Model 3700 gas chromatograph equipped with a capillary injector, an FID detector and a rubidium bead AFD detector. A 30 m x 0.25 mm I.D. glass capillary SE-30 WCOT column was used. The

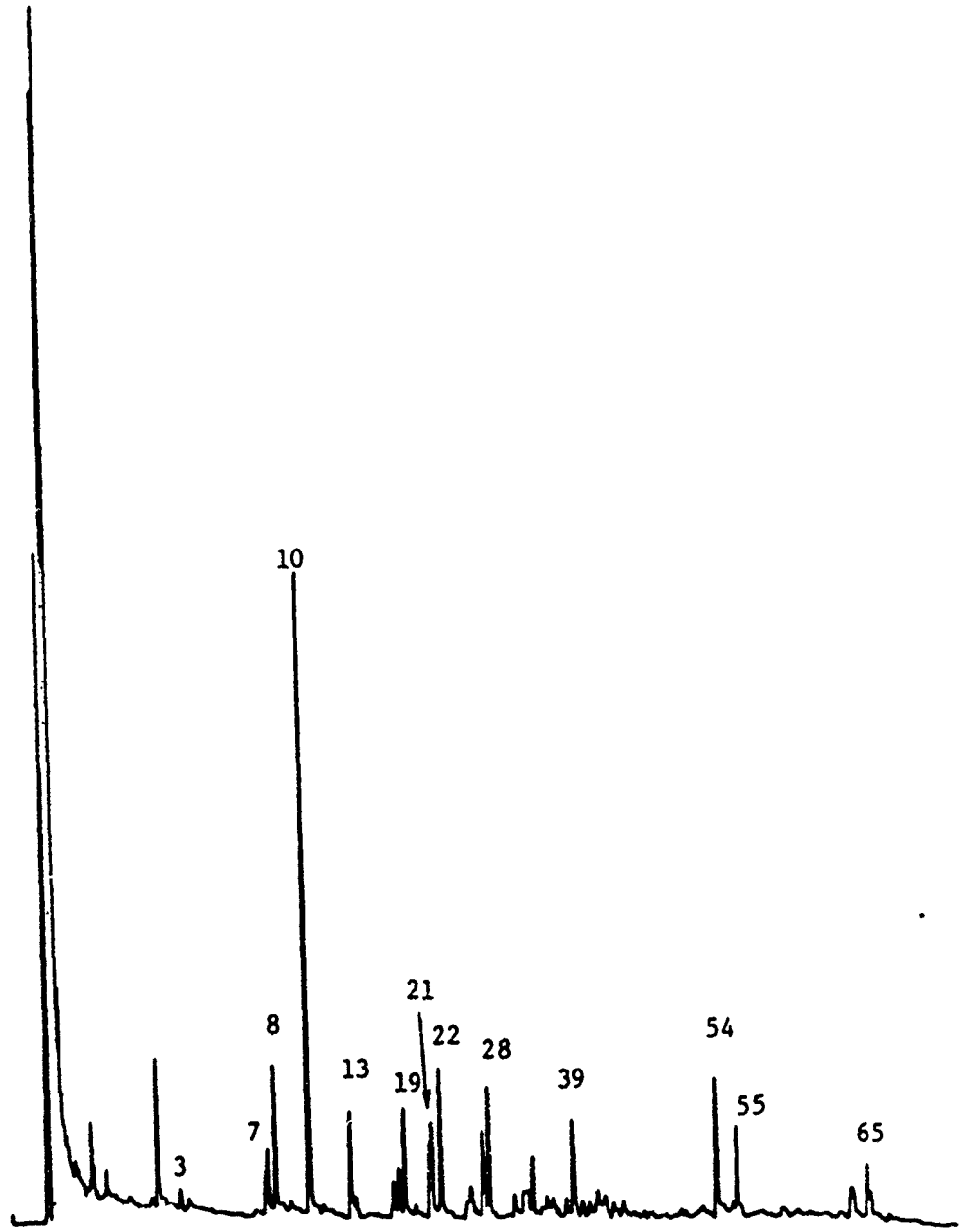


Figure 20. GC-PID Chromatogram of 0.5% Solution of Specification JP-4 in Pentane. (See Table 2 for tentative identification of numbered components)

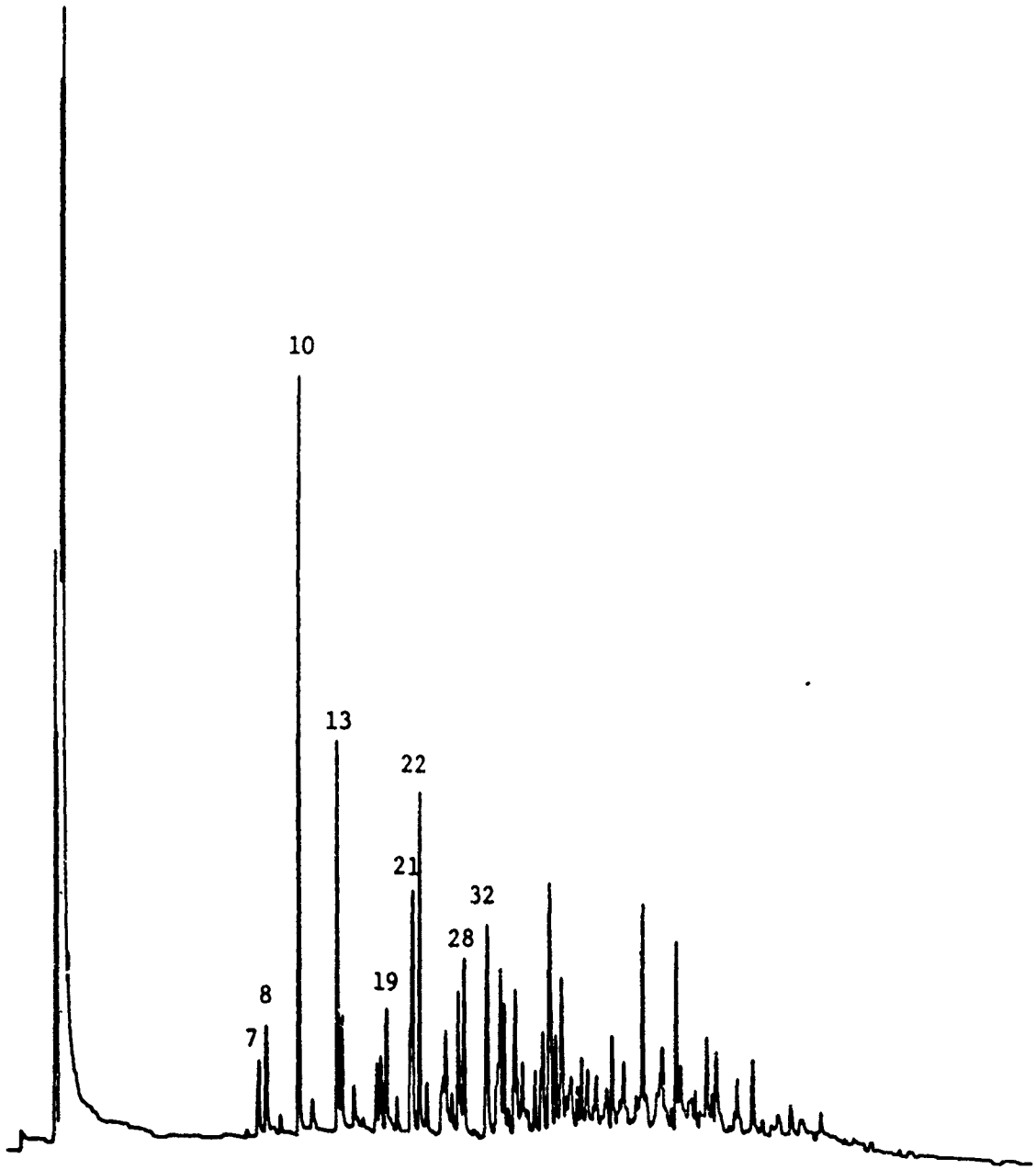


Figure 21. GC-PID Chromatogram of 0.5% Solution of Shale Oil JP-8 in Pentane. (See Table 2 for tentative identification of numbered components)

column was fitted at the effluent end with a glass-lined stainless steel splitter assembly that provided for the addition of makeup gas and a 1:1 split to the FID and AFD. Helium was used for a carrier gas flow of about 2 ml/min and makeup gas flow of 60 ml/min. Samples were introduced with an injector split ratio of 10:1.

Standard solutions containing various amounts of aromatic hydrocarbons, saturated hydrocarbons, and heterocyclic nitrogen-containing compounds were analyzed to obtain an indication of the relative AFD responses. The relative responses found for these three classes of compounds were approximately 1:5:10,000, i.e. saturated hydrocarbons gave 5 times the response of aromatic hydrocarbons, and nitrogen heterocyclics gave 2000 times the response of saturated hydrocarbons. The AFD detector was, therefore, selective for nitrogen-containing compounds but not sufficiently selective to avoid interference from large amounts of hydrocarbons. The detector can readily measure nitrogen-containing compounds in solution at a level of 0.2 µg/ml; however, a saturated hydrocarbon present at a level of 400 µg/ml or an aromatic hydrocarbon present at a level of 2,000 µg/ml would give the same response.

Several fuels supplied for this research program were analyzed using the FID/AFD system described above. The fuels were dissolved in heptane to give 10% solutions and 2 µl was injected. The FID was attenuated at 8×10^{-8} and the AFD was attenuated at 2×10^{-12}. Representative chromatograms obtained are given in Figures 22 to 25. The solutions of the JP-4/aromatic-solvent blend and Specification JP-8 gave no indication of concentrations of nitrogen compounds at levels above 0.2 µg/ml since all of the peaks in the AFD chromatograms can be accounted for as hydrocarbons in the FID chromatograms. By comparing the FID and AFD chromatograms for the JP-4/aromatic-solvent blend (Figure 22) it is seen that all of the major peaks in the AFD chromatogram are even larger peaks in the FID chromatogram and are therefore hydrocarbons rather than nitrogen-containing compounds. From the retention time pattern the components were identified as naphthalenes. In a similar manner, the chromatogram for the Specification JP-8 (Figure 23) indicates that the major peaks in the AFD chromatogram are saturated hydrocarbons, mainly normal paraffins, rather than nitrogen-containing compounds.

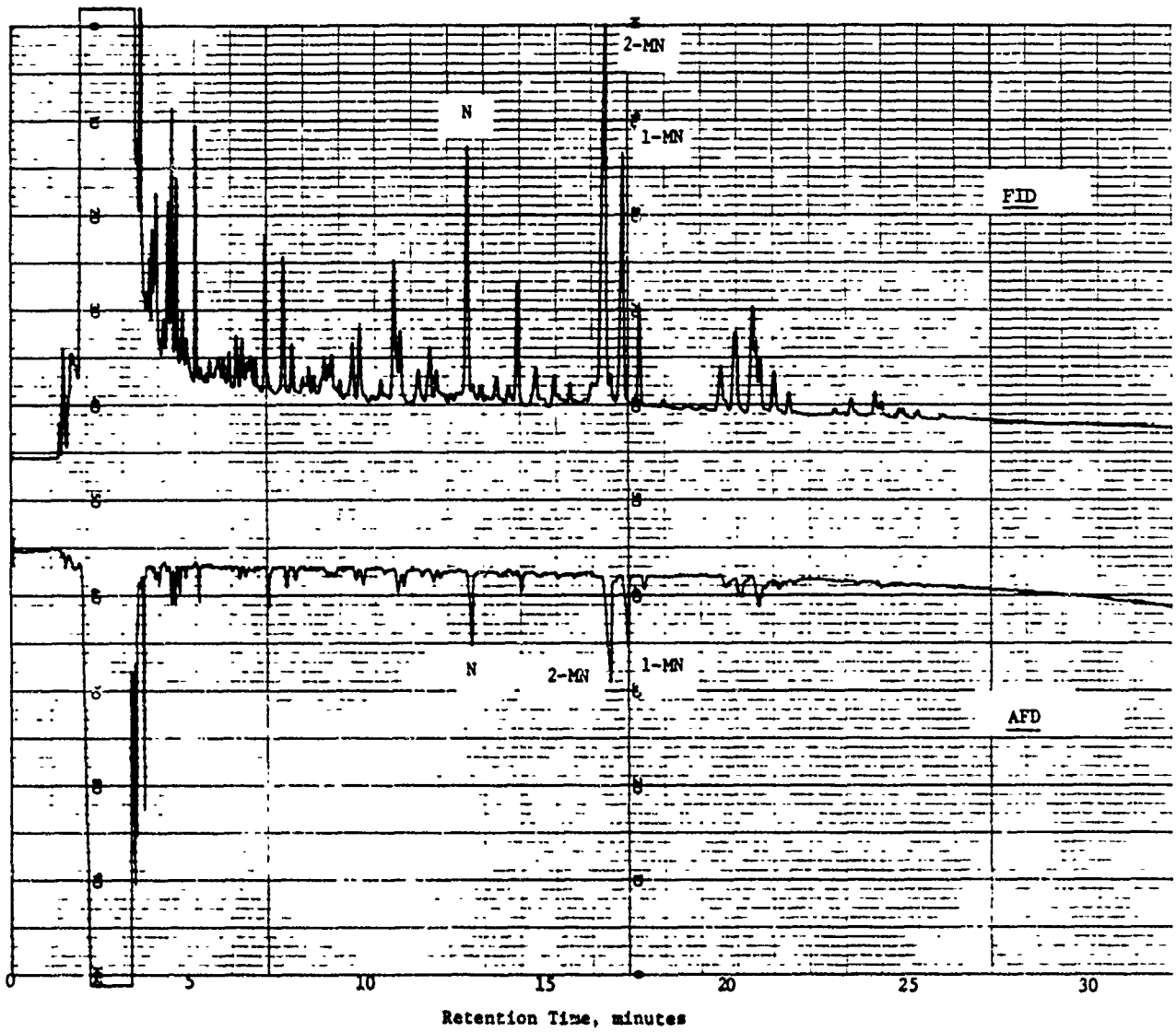


Figure 22. FID/AFD Gas Chromatogram of JP-4/Aromatic-Solvent Blend (N=naphthalene; MN=methylnaphthalene)

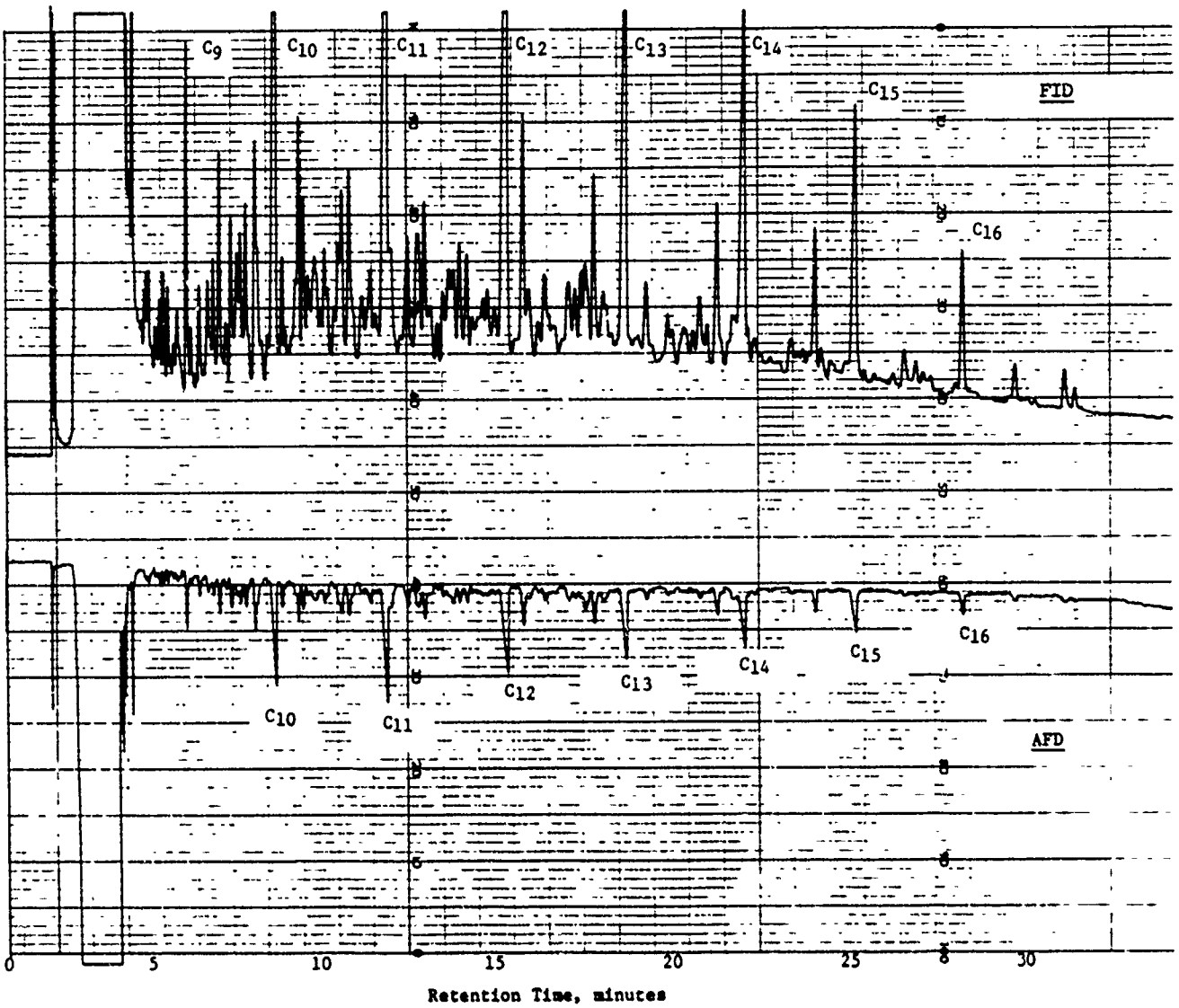


Figure 23. FID/AFD Gas Chromatogram of Specification JP-8 (C_9 to C_{16} are normal paraffins).

On the other hand, the chromatograms for the Shale Oil JP-4 and Syncrude Jet A (Figures 24 and 25) show specific major peaks in the AFD chromatograms that do not correspond to peaks in the FID chromatograms and hence can be attributed to nitrogen-containing compounds. Some of the nitrogen compounds appear to be present in the solution at levels near 10 µg/ml which corresponds to about 100 ppm in the fuel.

2. Extraction and GC-MS Studies

In order to identify the nitrogen-containing components detected by GC-AFD, the basic components of Syncrude Jet A were extracted and analyzed by GC-MS. An 800-ml sample of non-clay-treated Syncrude Jet-A was equilibrated with 800 ml of 1N H_2SO_4. The acid layer was withdrawn and washed with 200 ml of petroleum ether. The acid layer was made alkaline by the addition of 350 ml of 10% NaOH, treated with 120g of NaCl to salt out the free bases, and back-extracted two times with 150-ml portions of peroxide-free ethyl ether. The combined ether extract was analyzed by GC-MS using a 30 m x 0.25 mm I.D. SE-30 WCOT glass capillary column. The total ion chromatogram obtained is shown in Figure 26. The chromatographic pattern was similar to that observed in the GC-AFD analysis of the whole fuel (Figure 25) and thus the GC-MS data were used to tentatively identify the nitrogen-containing components in the whole fuel as well as in the extract. The MS data indicated that nearly all of the components were indeed nitrogen-containing compounds and were alkylpyridines or alkylquinolines. No pyrroles or indoles were detected. The tentative identification of the major components and the characteristic ions are given in Table 12.

3. HPLC-UV Studies

High-pressure liquid chromatography (HPLC) with an ultraviolet detector was applied to the fractionation of basic components of Syncrude Jet A in an effort to concentrate any pyrroles or indoles

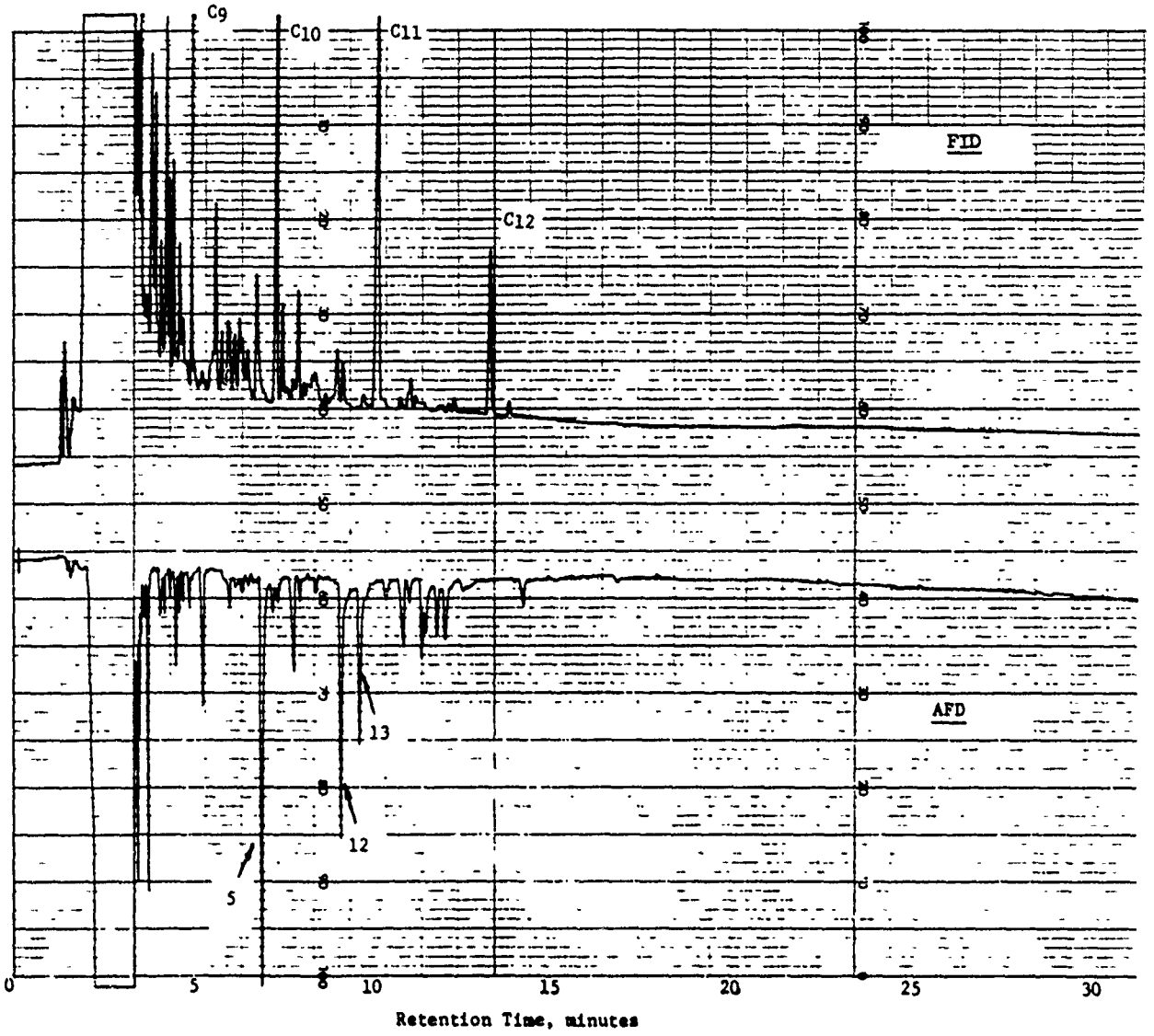


Figure 24. FID/AFD Gas Chromatogram of Shale Oil JP-4. (See Table 12 for identification of numbered components).

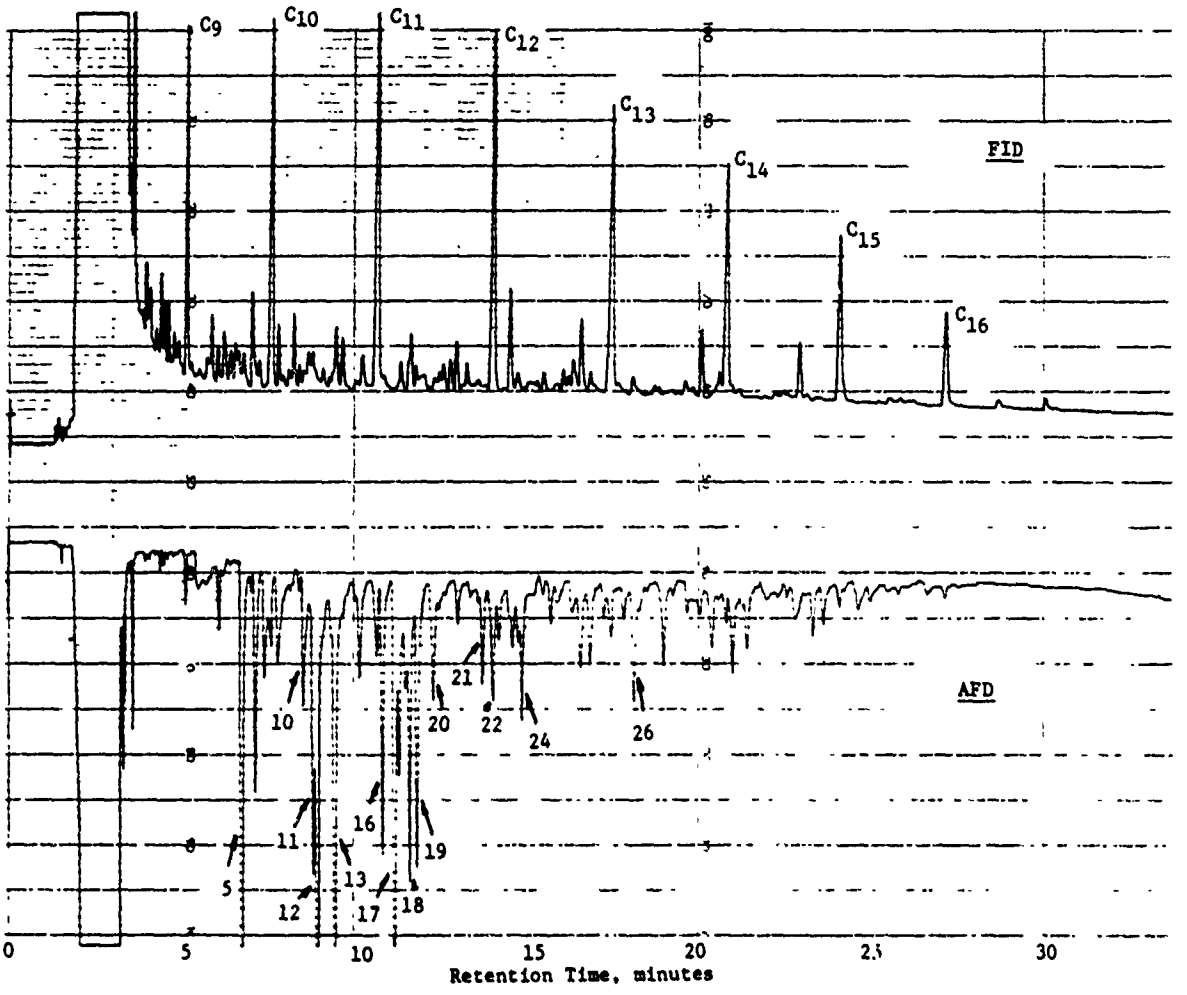


Figure 25. FID/AFD Gas Chromatogram of Syncrude Jet-A. (See Table 12 for identification of numbered components).

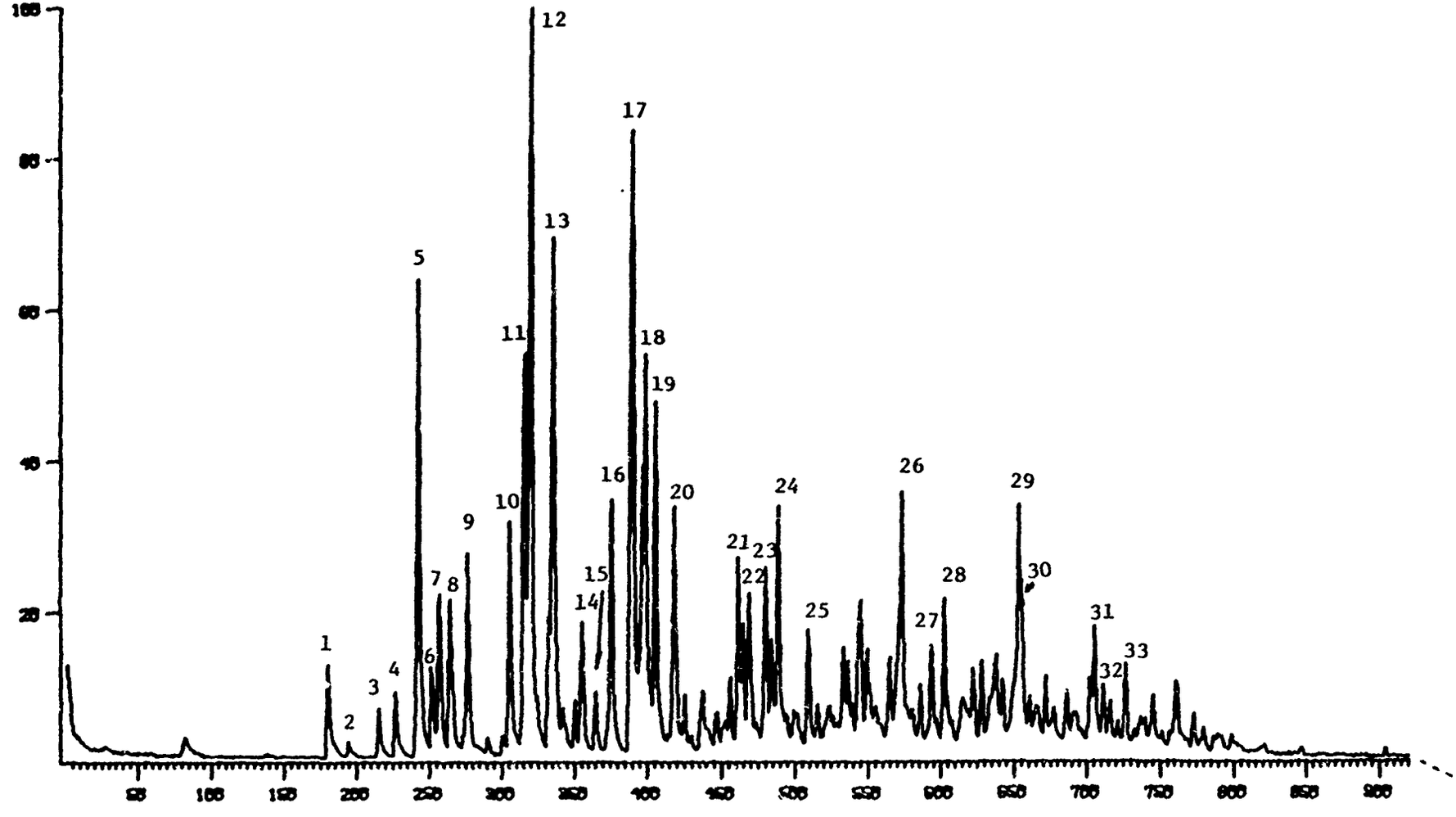


Figure 26. GC-MS Total Ion Chromatogram of the Basic Fraction of Syncrude Jet A
(Tentative identifications of the numbered components are given in Table 12)

TABLE 12. BASIC COMPONENTS EXTRACTED FROM SYNCRUDE JET A

GC Peak No.[a]	Tentative Identification	M.W.	Characteristic Ions in Mass Spectrum, m/e (relative intensity)			
1	C_2-Pyridine	107	107(100)	106(55)	92(23)	79(39)
2	C_2-Pyridine	107	107(100)	106(79)	92(27)	79(31)
3	C_3-Pyridine	121	121(46)	120(100)	106(6)	93(27)
4	C_2-Pyridine	107	107(100)	106(67)	92(30)	79(48)
5	C_3-Pyridine	121	121(100)	120(30)	106(19)	79(35)
6	C_2-Pyridine	107	107(100)	106(69)	92(31)	79(52)
7	C_3-Pyridine	121	121(100)	120(86)	106(14)	79(42)
8	C_3-Pyridine	121	121(46)	120(100)	93(23)	92(13)
9	C_3-Pyridine	121	121(100)	120(34)	106(53)	79(29)
10	C_3-Pyridine	121	121(100)	120(61)	106(35)	79(43)
11	C_3-Pyridine	121	121(100)	120(60)	106(31)	79(37)
12	C_4-Pyridine	135	135(52)	134(100)	107(28)	106(13)
13	C_4-Pyridine	135	135(100)	134(42)	120(47)	106(10)
14	C_5-Pyridine	149	149(7)	148(14)	135(26)	134(100)
15	C_4-Pyridine	135	135(66)	120(29)	107(100)	106(67)
16	C_4-Pyridine	135	135(100)	134(73)	120(39)	79(51)
17	C_5-Pyridine	149	149(18)	148(33)	135(100)	134(58)
18	C_5-Pyridine	149	149(5)	148(15)	135(58)	134(100)
19	C_5-Pyridine	149	149(41)	148(100)	133(18)	121(22)
20	C_5-Pyridine	149	149(32)	134(22)	121(100)	120(23)
21	C_5-Pyridine	149	149(41)	148(100)	121(21)	107(16)
22	C_6-Pyridine	163	163(44)	162(100)	135(34)	120(42)
23	C_6-Pyridine	163	163(2)	162(8)	148(18)	135(100)
24	C_5-Pyridine	149	148(6)	134(18)	121(100)	120(6)
25	C_6-Pyridine	163	163(13)	134(6)	121(100)	120(15)
26	C_7-Pyridine	177	177(1)	148(17)	134(20)	121(100)
27	C_7-Pyridine	177	177(6)	146(10)	134(8)	121(100)
28	C_2-Quinoline	157	157(100)	156(41)	143(36)	115(30)
29	C_7-Pyridine	177	162(2)	148(13)	134(17)	121(100)
30	C_2-Quinoline	157	157(100)	156(20)	142(12)	115(28)
31	C_3-Quinoline	171	171(100)	156(21)	128(15)	115(9)
32	C_3-Quinoline	171	171(100)	156(42)	128(29)	115(18)
33	C_7-Pyridine	177	176(2)	148(12)	134(19)	121(100)

a. See Figure 26.

that may be present. The HPLC system used in the study was comprised of the following components:

Pump: Altex Model 110A to give flow rate to 3 ml/min.

Injector: Micromeritics Model 725 automatic injector with a 10-µl sample loop, or
Altex Model 210 sample valve with 20-µl and 50-µl sample loops.

Detector: LDC Spectro Monitor III variable wavelength UV detector.

Columns: 25-cm x 0.46-cm I.D.

Normal-phase systems were chosen instead of reverse-phase systems in order to allow the nonpolar bulk of the material, the hydrocarbons, to elute first. Also the solvents suitable for normal-phase systems are more compatible with jet fuels than the aqueous-based solvent mixtures required for reverse-phase systems. The following three different normal-phase column packing materials were evaluated.

1. Spherisorb SI-5, a 5-µm silica obtained from Phase Separations, Ltd.
2. Zorbax-CN, a 5-µm cyano bonded phase obtained from duPont.
3. Lichrosorb-NH_2, a 10-µm amino bonded phase obtained from Merck.

Model compounds were studied that were representative of benzenes, naphthalenes, pyrroles, pyridines, indoles, and quinolines. The specific compounds and the abbreviations used for referring to them are given below:

1. 1,2,4,5-Tetramethylbenzene (TMB)
2. Naphthalene (N)
3. 2,3,6-Trimethylnaphthalene (TMN)
4. 2,5-Dimethylpyrrole (DMPL)
5. Pyridine (P)
6. 4-Methylpyridine (MP)
7. 2,6-Dimethylpyridine (2,6-DMP)
8. 3,5-Dimethylpyridine (3,5-DMP)
9. 2,4,6-Trimethylpyridine (TMP)
10. 7-Methylindole (MI)
11. 2-Methylquinoline (MQ)

Standard solutions of the individual compounds or mixtures were prepared in 10% THF in hexane or in the specific mobile phase at a concentration of 100 µg/ml.

A 10% solution of jet fuel in n-hexane was used for the study. The specific jet fuel sample was Syncrude Jet A (non-clay-treated), PCH-79-268-C.

A diethyl ether extract containing the basic components of the above jet fuel was also studied. This extract was the same one that was prepared for the GC-MS study of nitrogen-containing components discussed previously.

The mobile phases studied were mixtures of methylene chloride, isopropyl alcohol, or tetrahydrofuran in n-hexane. The mixtures were prepared with and without the addition of small amounts of triethylamine. The tetrahydrofuran was passed through activated alumina to remove peroxides prior to use.

The three columns with various mobile phases were evaluated for the separation of the model compounds. The mobile-phase composition was adjusted to give the best possible selectivity with capacity factors (K') varying between 1 and 10 if possible. A detector wavelength setting of 260 nm was used in most cases since that approximates the wavelength maxima for the pyridines, quinolines and indoles.

The amino bonded-phase column gave the best performance in terms of peak shape and selectivity. The cyano bonded-phase column and silica column could not be used because of very severe peak tailing.

An article by Wheals and White (J. Chromatog. 176 421 (1979)) indicated that in situ modification of a silica gel column with an amine can give a column that performs similarly to an amino bonded-phase column. If this approach would work for use with the model compounds of interest in this study, a relatively inexpensive preparative silica column could be prepared for the fractionation of large quantities of jet fuels. Therefore the procedure was tried with a Spherisorb SI-5 column using triethylamine. A solution containing 0.1% triethylamine in 50:50 methanol:hexane was passed through the column at 3 ml/min for 40 minutes. The column was equilibrated prior to use with a mobile phase containing 0.01% triethylamine.

Triethylamine was also added to the mobile phase when the amino bonded-phase column was used because it improved the peak shape for 2,4,6-trimethylpyridine and had a strong effect upon the retention times. For example, the addition of 0.01% triethylamine to a mobile phase containing 50% CH_2Cl_2 in n-hexane decreased the retention time for 2,4,6-trimethylpyridine from 35 minutes to 5.6 minutes. The addition of more than 0.05% triethylamine gave excessive baseline instability.

The capacity factors obtained for model compounds using four representative sets of conditions are given in Table 13. Condition Set A, a Lichrosorb-NH_2 column with 30% CH_2Cl_2 and 0.01% triethylamine in n-hexane,

TABLE 13. HPLC SEPARATION OF MODEL COMPOUNDS

Compound	Capacity Factors, K', Using Given Conditions[a] A	B	C	D
1,2,4,5-Trimethylbenzene	0.08	0.07	ND	0.09
Naphthalene	0.17	0.15	ND	ND
2,3,6-Trimethylnaphthalene	0.13	0.10	ND	ND
2,5-Dimethylpyrrole	1.45	2.47	ND	0.56
Pyridine	ND[b]	ND	4.75	ND
4-Methylpyridine	ND	ND	6.02	ND
2,6-Dimethylpyridine	ND	ND	3.68	ND
3,5-Dimethylpyridine	ND	ND	4.74	ND
2,4,6-Trimethylpyridine	8.14	3.20	5.05	8.16
7-Methylindole	4.12	7.59	ND	1.07
2-Methylquinoline	6.10	2.58	ND	5.85

a. A = Lichrosorb-NH_2; 30% CH_2Cl_2 + 0.01% TEA in n-hexane; RT_o = 1.10 min
B = Lichrosorb-NH_2; 0.5% iPrOH + 0.01% TEA in n-hexane; RT_o = 1.10 min
C = Lichrosorb-NH_2; 60% CH_2Cl_2 + 0.01% TEA in n-hexane; RT_o = 1.10 min
D = Spherisorb SI-5; 40% CH_2Cl_2 + 0.04% TEA in n-hexane; RT_o = 1.00 min

b. Not determined.

was considered the best and was selected for studying jet fuel and the basic extract. These conditions provide good separation of pyrroles and indoles from the non-polar hydrocarbons and the more polar pyridines and quinolines. The calculated number of theoretical plates achieved for the 2,4,6-trimethylpyridine peak was 4,000. The column was found to be quite stable in this application since several dozen injections of jet fuel and its basic extract did not change the performance characteristics.

The modified silica column, Condition Set D, gave separations similar to those of Set A, however, the K' values for 2,5-dimethylpyrrole and 7-methylindole were unacceptably low. The use of less methylene chloride or a different amine might give more favorable results. The results from Set C were included to show that all of the various pyridines gave rather similar K' values. It was, therefore, considered sufficient to use 2,4,6-trimethylpyridine to represent all of the pyridines in subsequent studies. The use of isopropyl alcohol instead of methylene chloride, Set B vs. Set A, changed the selectivity pattern very significantly. The pyrrole and indole were retained more strongly and the pyridine and quinoline retained less strongly than when methylene chloride was used. Consequently pyrroles and indoles cannot be separated from pyridines and quinolines under those conditions.

The separation of five model compounds using the preferred conditions, Set A, is shown by the chromatogram in Figure 27. The fractionation of jet fuel and an extract containing the corresponding basic components under those same conditions is shown by the chromatograms in Figures 28 and 29, respectively. A comparison of these latter two chromatograms shows that the pattern is very similar in both cases except that the whole jet fuel gives a large peak within the first two minutes which represents a composite of all of the aromatic hydrocarbons present. Thus the system can be used to give a fingerprint that provides qualitative and quantitative information on the trace amounts of basic components in whole jet fuel without resorting to an acid extraction.

In an effort to characterize the various basic components, twelve HPLC fractions of the basic extract were collected and analyzed by GC-MS using a 30-m x 0.25-mm I.D. SE-52 glass capillary column. The retention time windows for each fraction are indicated in Figure 29. A Finnigan Model 4000 quadrupole mass spectrometer interfaced with a

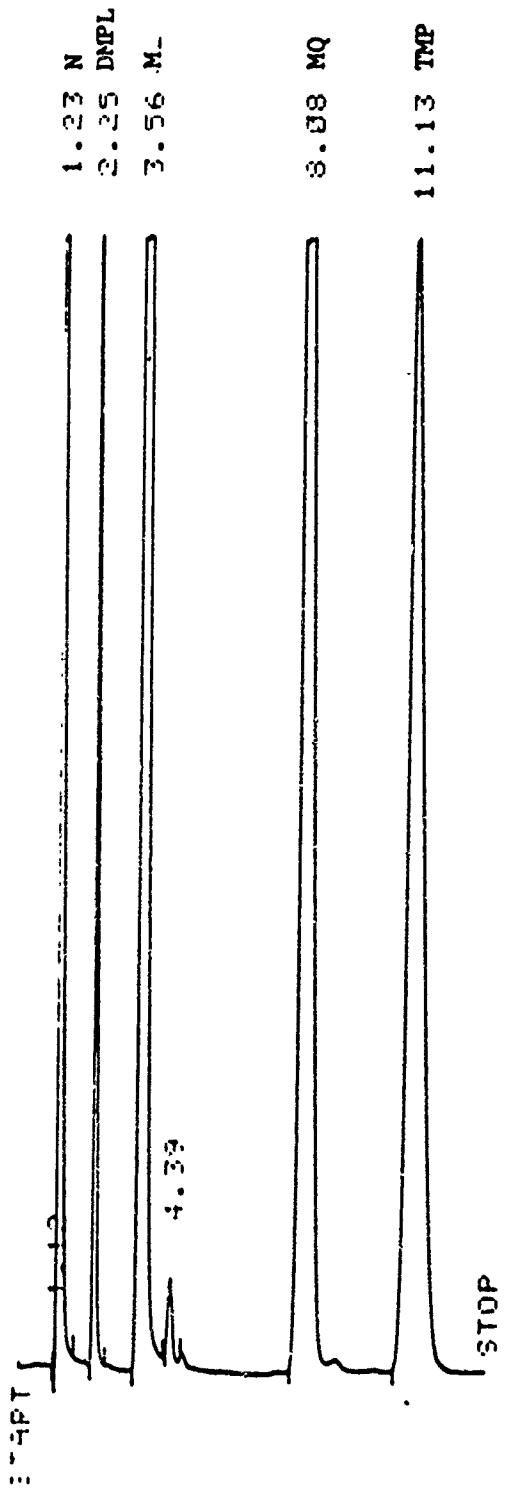


Figure 27. HPLC Chromatogram of Model Compounds.

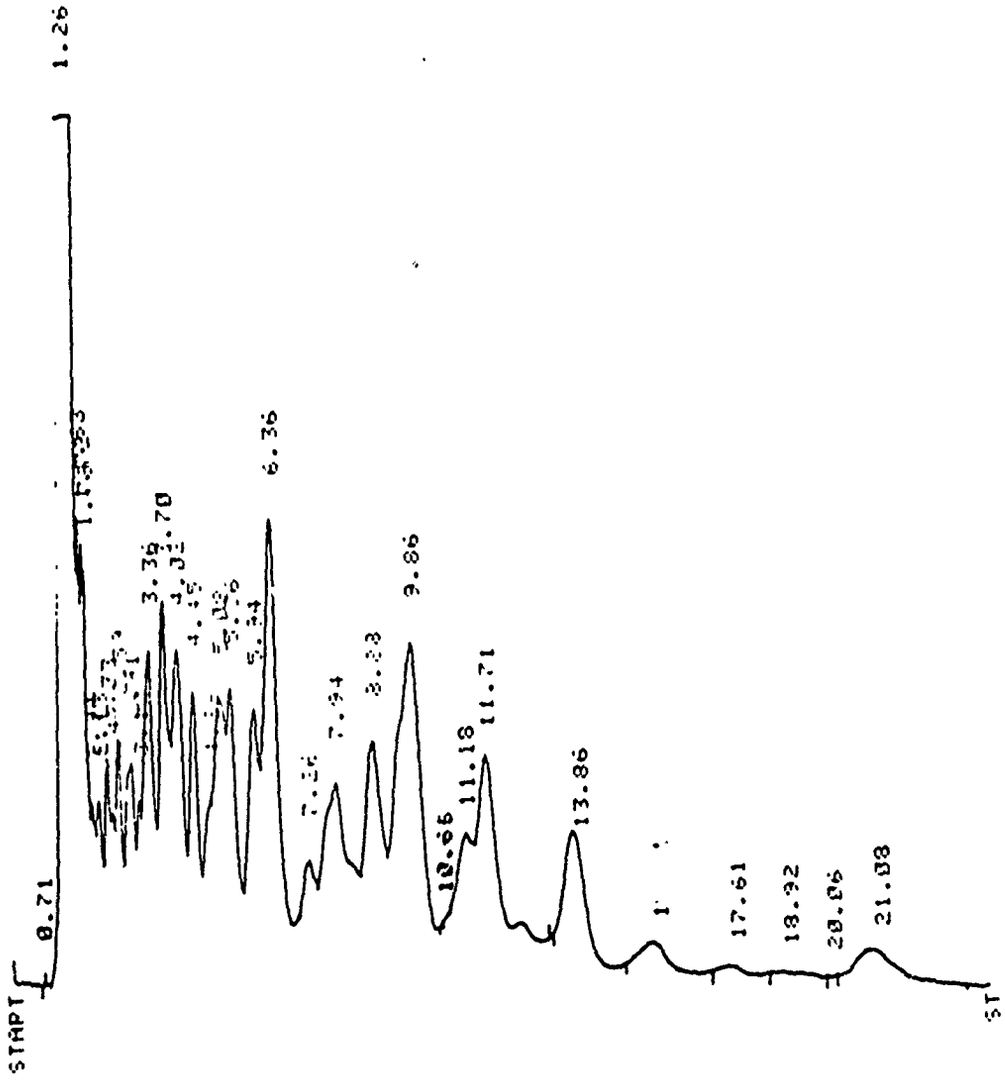


Figure 28. HPLC Cnromatogram of Syncrude Jet A

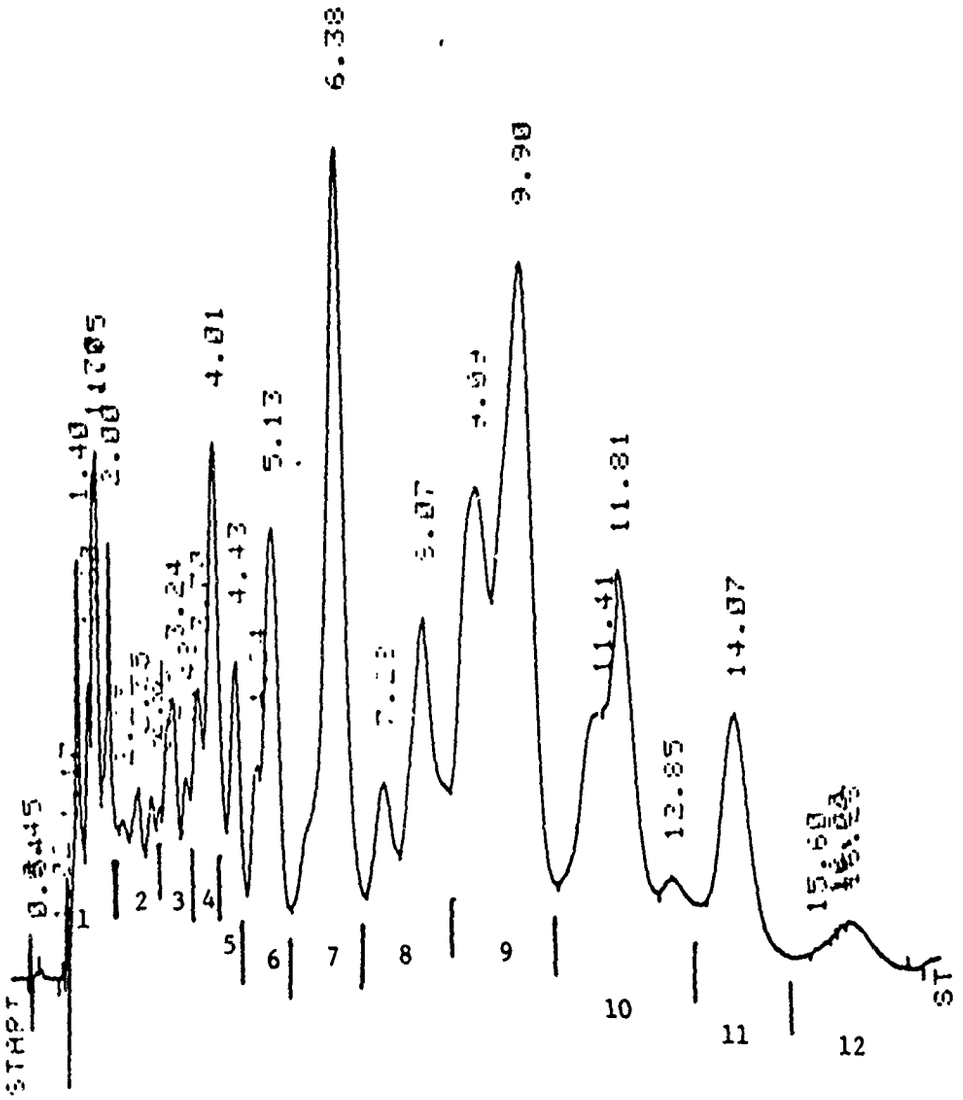


Figure 29. HPLC Chromatogram of the Basic Fraction of Syncrude Jet A

Finnigan Model 9610 gas chromatograph and an INCOS data system was used for the study. The samples were analyzed both in the chemical ionization (CI) mode with isobutane as the ionizing gas as well as in the electron impact (EI) mode. Analysis in the CI mode was necessary to verify the molecular weights of the more highly alkylated compounds which fragmented so much under EI conditions that the molecular ions were not readily discernible.

The major individual compounds in each HPLC fraction were tentatively identified on the basis of molecular weight and EI fragmentation pattern. A total of 145 different compounds were tentatively identified. In most cases, a given compound was found in only one HPLC fraction; however, occasionally a compound was present in two consecutive fractions indicating that it eluted from the HPLC column at the same time that a fraction change was made.

The tentatively identified compounds included alkylpyridines, alkylanilines, alkylquinolines, alkylisoquinolines, alkyltetrahydroquinolines, alkyltetrahydroisoquinolines, and a tetrahydroacridine. The pyridines and anilines with identical molecular weights were differentiated on the basis of GC retention time which is dependent upon boiling point. In general, an aniline with a given molecular weight will have a boiling point similar to that of a pyridine with a molecular weight that is 28 higher. For example, a methylaniline, m.w. 107, will have approximately the same boiling point as a tetramethylpyridine, m.w. 135. The quinolines and isoquinolines with the same molecular weights were differentiated on the basis of the HPLC fraction number which was dependent upon basicity. In general, isoquinolines are more basic than quinolines and thus would be expected to elute from the HPLC column in the later fractions. Similarly, tetrahydroquinolines were differentiated from tetrahydroisoquinolines. It should be emphasized that all of the identifications given are tentative. Other isomers, such as aminonaphthalenes instead of quinolines, are possible. Reference compounds and/or other analytical methods, such as infrared spectroscopy, would need to be studied to confirm the identifications.

A summary of the numbers of different compounds found in each HPLC fraction is given in Table 14. Although there are certain distribution trends, e.g. quinolines and anilines eluting from the HPLC column earlier than the pyridines, there is a considerable amount of overlap which reflects the different properties of different isomers. No pyrroles or indoles were detected; if any such compounds were present, their concentrations were extremely low.

The reconstructed gas chromatograms obtained from the GC-EIMS analysis of the twelve HPLC fractions, which show the complexity of the fractions, are given in Figures D-1 to D-12 in Appendix D. A complete list of the 145 individual compounds tentatively identified along with their GC-MS scan number, molecular weight verified by CIMS, and HPLC fraction number is given in retention time order (scan number order) in Table 15. The data available do not permit the 33 tentative identifications in Table 12 to be correlated with those in Table 15. The EI mass spectra of the various isomers were quite distinct. For example, Compounds 28 and 29 (in Table 15) which are both C_4-pyridines and which have identical GC retention times elute in HPLC Fractions 10 and 12, respectively and have the distinctly different mass spectra shown in Figures 30 and 31. Similarily, Compounds 48 and 49 which are both C_5-pyridines and which have identical GC retention times elute in HPLC Fractions 11 and 3, respectively, and have the distinctly different mass spectra shown in Figures 32 and 33. It is, therefore, apparent that the GC-MS detection of the 145 compounds in Table 15 would not be possible without the use of HPLC fractionation.

TABLE 14. SUMMARY OF COMPOUNDS FOUND IN HPLC FRACTIONS FROM THE BASIC FRACTION OF SYNCRUDE JET A

Compound Type	Molecular Weight	Total No. of Isomers Found	Number of Isomers Found in Given HPLC Fraction											
			1	2	3	4	5	6	7	8	9	10	11	12
C_1-Aniline	107	1				1								
C_2-Aniline	121	1			1									
C_3-Aniline	135	2		2										
C_4-Aniline	149	3		3										
C_3-Pyridine	121	9					1	1	1	1	3	2	3	3
C_4-Pyridine	135	13			1	1	1	1	1	3	2	3	2	3
C_5-Pyridine	149	17		2	3	3	2	2	2	2	1	1	1	1
C_6-Pyridine	163	18		3	2	3	4	2	3	1		1		
C_7-Pyridine	177	14		5	3	1	2	2	2	1	1	1		
C_8-Pyridine	191	11		2	1	2	3	1	1		1			
C_9-Pyridine	205	7		2	1	2		1	1		1			
C_{10}-Pyridine	219	5		2	2				1					
C_2-Quinoline	157	4	1	1	1	1	1							
C_3-Quinoline	171	6	4	3	2									
C_4-Quinoline	185	5	5	1										
C_1-Isoquinoline	143	3								2			1	
C_2-Isoquinoline	157	6								3	1	1		1
C_3-Isoquinoline	171	5						1	1	2		1	1	
C_1-Tetrahydroquinoline	147	1									1			
C_2-Tetrahydroquinoline	161	1							1	1				
C_3-Tetrahydroquinoline	175	6				1	1	3	1	1				
C_4-Tetrahydroquinoline	189	1								1				
C_1-Tetrahydroisoquinoline	147	2												?
C_2-Tetrahydroisoquinoline	161	3												3
Tetrahydroacridine	183	1		1										

TABLE 15. NITROGEN-CONTAINING AROMATIC COMPOUNDS FOUND IN HPLC FRACTIONS FROM THE BASIC FRACTION OF SYNCRUDE JET A.

Compound No.	GC-MS Scan No.	M.W.	Tentative Identification	HPLC Fraction No.
1	524	121	C_3-Pyridine-1	5+6
2	559	121	C_3-Pyridine-2	10+11
3	581	121	C_3-Pyridine-3	8+9
4	591	121	C_3-Pyridine-4	9+10
5	600	121	C_3-Pyridine-5	7
6	604	121	C_3-Pyridine-6	9
7	608	121	C_3-Pyridine-7	11+12
8	634	135	C_4-Pyridine-1	3
9	647	135	C_4-Pyridine-2	4
10	648	121	C_3-Pyridine-8	11+12
11	662	121	C_3-Pyridine-9	12
12	666	107	C_1-Aniline-1	4
13	665	135	C_4-Pyridine-3	5
14	670	135	C_4-Pyridine-4	7+8
15	691	135	C_4-Pyridine-5	10
16	695	149	C_5-Pyridine-1	2
17	696	135	C_4-Pyridine-6	6
18	702	135	C_4-Pyridine-7	8
19	714	135	C_4-Pyridine-8	8
20	721	135	C_4-Pyridine-9	9
21	724	149	C_5-Pyridine-2	4
22	734	135	C_4-Pyridine-10	11+12
23	746	149	C_5-Pyridine-3	2
24	751	149	C_5-Pyridine-4	3
25	764	135	C_4-Pyridine-11	11+12
26	767	149	C_5-Pyridine-5	5
27	770	149	C_5-Pyridine-6	4
28	776	135	C_4-Pyridine-12	10
29	776	135	C_4-Pyridine-13	12
30	777	149	C_5-Pyridine-7	3
31	777	121	C_2-Aniline-1	3
32	782	149	C_5-Pyridine-8	3
33	783	149	C_5-Pyridine-9	6+7

TABLE 15. (Continued)

Compound No.	GC-MS Scan No.	M.W.	Tentative Identification	HPLC Fraction No.
34	790	149	C_5-Pyridine-10	7+8
35	806	149	C_5-Pyridine-11	5
36	807	149	C_5-Pyridine-12	10
37	809	149	C_5-Pyridine-13	4
38	812	163	C_6-Pyridine-1	2
39	822	163	C_6-Pyridine-2	3
40	833	163	C_6-Pyridine-3	5
41	835	163	C_6-Pyridine-4	4
42	838	149	C_5-Pyridine-14	6
43	850	163	C_6-Pyridine-5	2
44	857	149	C_5-Pyridine-15	9
45	862	149	C_5-Pyridine-16	8
46	862	163	C_6-Pyridine-6	7
47	868	163	C_6-Pyridine-7	2
48	872	149	C_5-Pyridine-17	11
49	872	149	C_5-Pyridine-8	3
50	876	163	C_6-Pyridine-9	4+5
51	883	135	C_3-Aniline-1	2
52	892	163	C_6-Pyridine-10	6
53	894	135	C_3-Aniline-2	2
54	899	163	C_6-Pyridine-11	5
55	900	163	C_6-Pyridine-12	7
56	902	163	C_6-Pyridine-13	4
57	902	163	C_6-Pyridine-14	6
58	903	177	C_7-Pyridine-1	2
59	910	177	C_7-Pyridine-2	2
60	920	177	C_7-Pyridine-3	2
61	922	177	C_7-Pyridine-4	3
62	929	163	C_6-Pyridine-15	10
63	934	147	C_1-Tetrahydroisoquinoline-1	12
64	937	163	C_6-Pyridine-16	5
65	938	149	C_4-Aniline-1	2
66	945	147	C_1-Tetrahydroquinoline-1	9

TABLE 15. (Continued)

Compound No.	GC-MS Scan No.	M.W.	Tentative Identification	HPLC Fraction No.
67	956	147	C_1-Tetrahydroisoquinoline-2	12
68	958	163	C_6-Pyridine-17	8
69	967	177	C_7-Pyridine-5	2+3
70	968	163	C_6-Pyridine-18	7
71	969	143	C_1-Isoquinoline-1	8
72	977	161	C_2-Tetrahydroquinoline-1	7+8
73	981	177	C_7-Pyridine-6	2+3
74	989	161	C_2-Tetrahydroisoquinoline-1	12
75	992	177	C_7-Pyridine-7	6
76	993	149	C_4-Aniline-2	2
77	999	149	C_4-Aniline-3	2
78	999	177	C_7-Pyridine-8	5
79	1009	161	C_2-Tetrahydroisoquinoline-2	12
80	1011	177	C_7-Pyridine-9	4+5
81	1014	177	C_7-Pyridine-10	7
82	1021	191	C_8-Pyridine-1	2
83	1026	175	C_3-Tetrahydroquinoline-1	6
84	1027	143	C_1-Isoquinoline-2	8
85	1039	177	C_7-Pyridine-11	9+10
86	1046	143	C_1-Isoquinoline-3	11
87	1053	157	C_2-Quinoline-1	1+2
88	1056	175	C_3-Tetrahydroquinoline-2	4+5
89	1068	157	C_2-Quinoline-2	5
90	1069	177	C_7-Pyridine-12	8
91	1072	191	C_8-Pyridine-2	3
92	1072	175	C_3-Tetrahydroquinoline-3	7
93	1073	177	C_7-Pyridine-13	6
94	1078	189	C_4-Tetrahydroquinoline-1	8
95	1080	175	C_3-Tetrahydroquinoline-4	6
96	1083	177	C_7-Pyridine-14	7
97	1085	191	C_8-Pyridine-3	2
98	1091	191	C_8-Pyridine-4	5
99	1096	157	C_2-Isoquinoline-1	8

TABLE 15. (Continued)

Compound No.	GC-MS Scan No.	M.W.	Tentative Identification	HPLC Fraction No.
100	1096	161	C_2-Tetrahydroisoquinoline-3	12
101	1098	191	C_8-Pyridine-5	6
102	1106	191	C_8-Pyridine-6	4
103	1117	191	C_8-Pyridine-7	5
104	1118	191	C_8-Pyridine-8	7
105	1118	157	C_2-Isoquinoline-2	8
106	1120	157	C_2-Isoquinoline-3	3
107	1120	191	C_8-Pyridine-9	4
108	1122	157	C_2-Isoquinoline-3	10
109	1124	175	C_3-Tetrahydroquinoline-5	6
110	1128	157	C_2-Isoquinoline-4	8
111	1140	157	C_2-Quinoline-4	4
112	1142	157	C_3-Quinoline-1	1
113	1145	191	C_8-Pyridine-10	9
114	1148	175	C_3-Tetrahydroquinoline-6	8
115	1154	157	C_2-Isoquinoline-5	9
116	1168	171	C_3-Quinoline-2	1+2
117	1168	205	C_9-Pyridine-1	2
118	1170	171	C_3-Isoquinoline-1	6
119	1171	157	C_2-Isoquinoline-6	12
120	1171	191	C_8-Pyridine-11	5
121	1186	205	C_9-Pyridine-2	2
122	1193	171	C_3-Quinoline-3	1+2
123	1196	205	C_9-Pyridine-3	6
124	1203	171	C_3-Quinoline-4	1+2
125	1207	205	C_9-Pyridine-4	4
126	1211	171	C_3-Isoquinoline-2	7
127	1219	205	C_9-Pyridine-5	7
128	1220	205	C_9-Pyridine-6	3+4
129	1232	171	C_3-Isoquinoline-3	8
130	1235	171	C_3-Quinoline-5	3
131	1235	171	C_3-Isoquinoline-4	10+11
132	1245	171	C_3-Isoquinoline-5	8

TABLE 15. (Continued)

Compound No.	GC-MS Scan No.	M.W.	Tentative Identification	HPLC Fraction No.
133	1245	205	C_9-Pyridine-7	9
134	1253	171	C_3-Quinoline-6	3
135	1253	185	C_4-Quinoline-1	1
136	1264	219	C_{10}-Pyridine-1	2
137	1272	185	C_4-Quinoline-2	1
138	1282	219	C_{10}-Pyridine-2	2
139	1296	185	C_4-Quinoline-3	1+2
140	1301	219	C_{10}-Pyridine-3	3
141	1302	183	Tetrahydroacridine-1	2
142	1310	185	C_4-Quinoline-4	1
143	1315	219	C_{10}-Pyridine-4	7
144	1317	219	C_{10}-Pyridine-5	3
145	1327	185	C_4-Quinoline-5	1

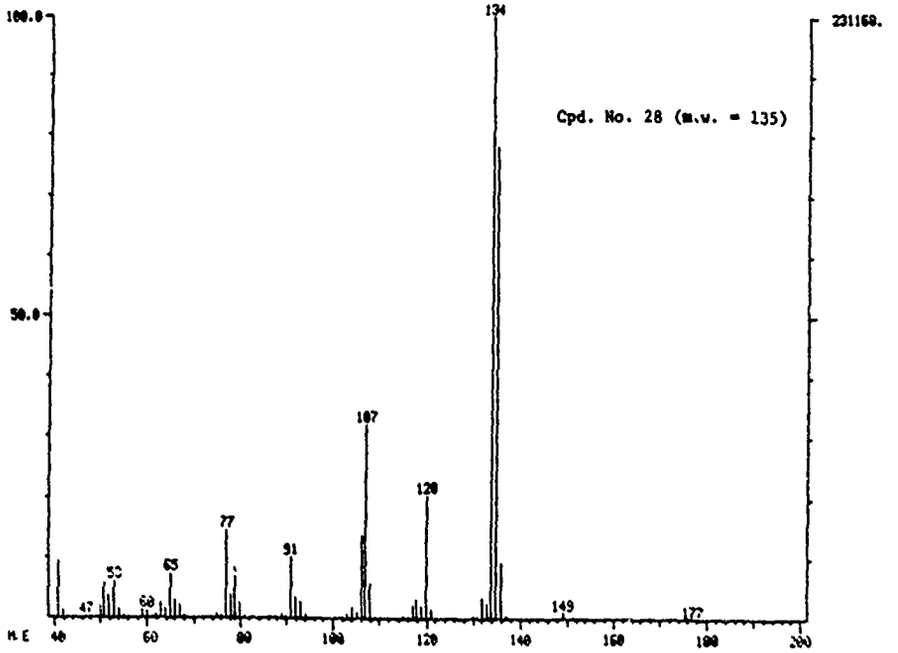


FIGURE 30. EI MASS SPECTRUM OF COMPOUND 28 FROM THE BASIC FRACTION OF SYNCRUDE JET A.

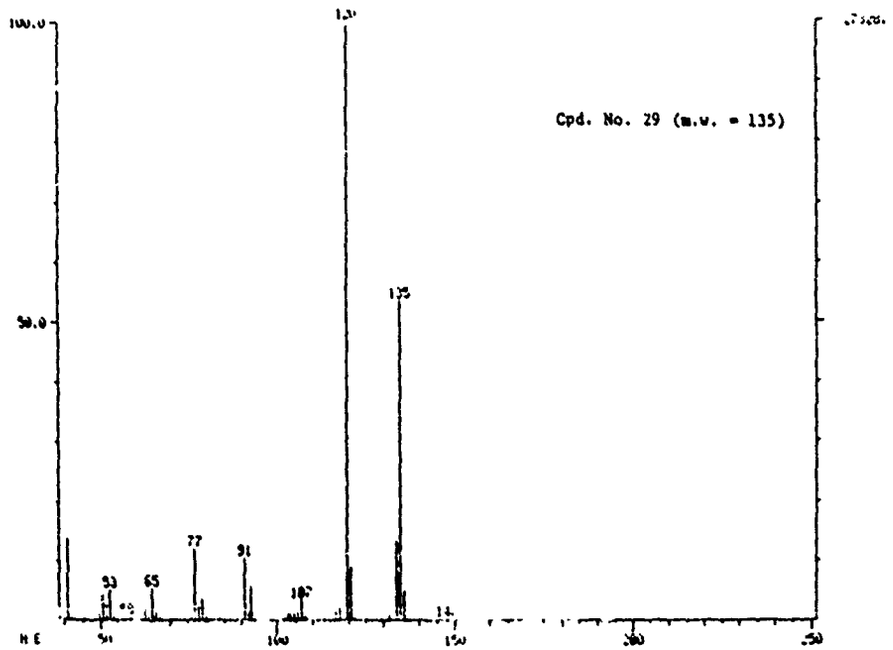


FIGURE 31. EI MASS SPECTRUM OF COMPOUND 29 FROM THE BASIC EXTRACT OF SYNCRUDE JET A.

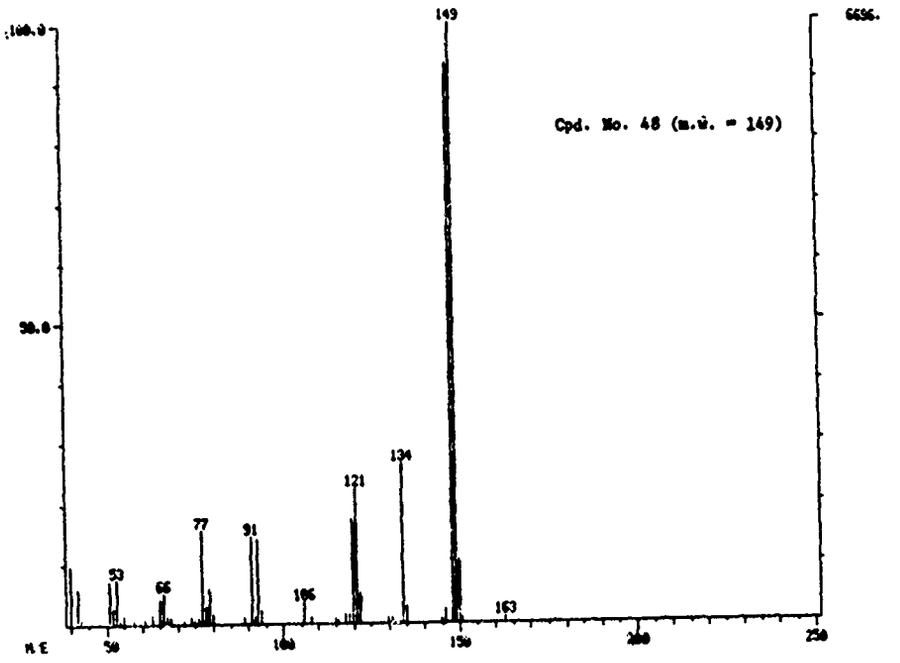


FIGURE 32. EI MASS SPECTRUM OF COMPOUND 48 FROM THE BASIC FRACTION OF SYNCRUDE JET A.

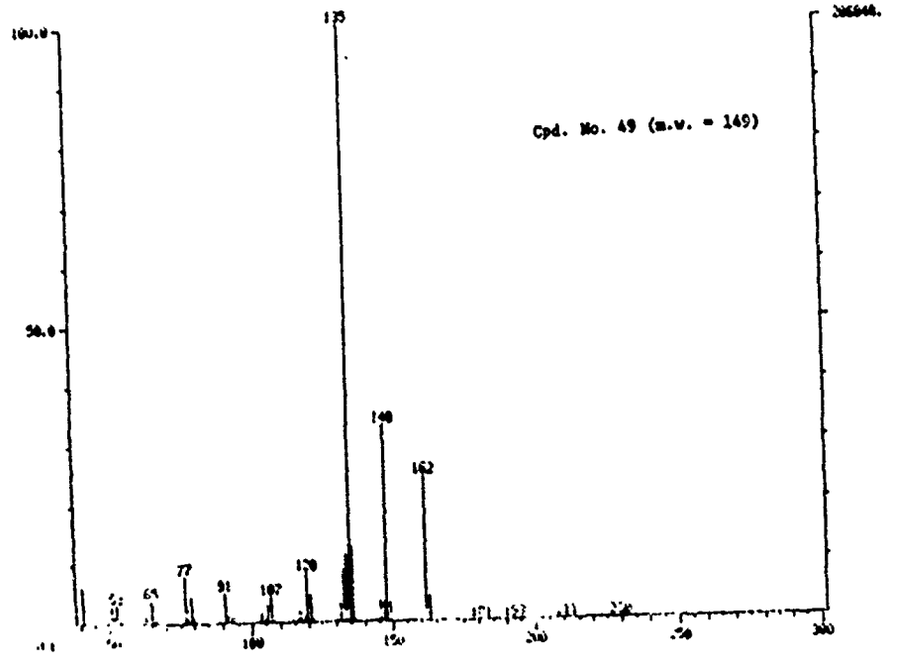


FIGURE 33. EI MASS SPECTRUM OF COMPOUND 49 FROM THE BASIC FRACTION OF SYNCRUDE JET A.

SECTION IV

RECOMMENDATIONS

A. SCOPE

The ultimate objective of the program is the recommendation of an integrated analysis scheme that will provide as much reliable information as possible, as rapidly and economically as possible, on the content of individual aromatic compounds in jet fuels. The methods studied during the program and several related methods have, therefore, been evaluated and compared in terms of the following ten performance areas:

Quantitative reliability
Qualitative reliability
Selectivity
Range of compounds detected
Sensitivity
Compound resolution
Linear range
Speed
Simplicity
Cost

In order to meet the objective stated above, the first seven areas, which are data quality concerns have been balanced against the last three areas, which are operational concerns. Thirteen candidate methods have been considered. Each method is one that might reasonably be considered for the analysis of aircraft fuels. All GC methods considered involve the use of high resolution glass or fused silica capillary columns. The major advantages and disadvantages of each method are discussed briefly below. The relative merits of each method are summarized in Table 16 in which a rating is given for each method in each area of performance.

TABLE 16. SUITABILITY OF VARIOUS ANALYTICAL METHODS FOR DETERMINING AROMATIC COMPOUNDS IN AIRCRAFT FUELS

Area of Performance	Estimated Rating(a) of Given Analytical Method												
	GC-UVD	GC-PID	GC-AFD	GC-FID	LC + GC-FID	LC + GC-FID	LC + GC-IR	LC + GC-MS	HPLC-UVD	HPLC + GC-UVD	HPLC + GC-FID	HPLC+ GC-IR	HPLC+ GC-MS
Quantitative Reliability	2	1	2	2	1	2	1	2	2	2	2	1	2
Qualitative Reliability	1	1	1	0	1	1	2	2	0	1	1	2	2
Selectivity	2	1	1	0	2	2	2	2	2	2	2	2	2
Range of Compounds	2	2	0	2	2	2	2	2	2	2	2	2	2
Sensitivity	2	2	2	2	2	2	0	2	2	2	2	2	2
Compound Resolution	1	1	1	1	1	1	1	1	0	2	2	2	2
Linear Range	1	1	2	2	1	2	1	1	1	1	2	1	1
Speed	2	2	2	2	1	1	1	1	2	0	0	0	0
Simplicity	2	2	2	2	1	1	1	1	2	0	0	0	0
Cost	2	2	2	2	1	1	0	0	2	0	0	0	0
TOTAL	17	15	15	15	13	15	11	14	15	12	13	12	13

(a) 0 = Poor; 1 = Good; 2 = Excellent

B. PERFORMANCE OF CANDIDATE METHODS

1. GC-UVD

The use of an ultraviolet detector for GC analysis has been shown in this program to have many attractive performance features. The major attractions of GC-UVD are the selectivity for aromatic compounds achieved and the speed, simplicity, and low cost of performance.

Like all chromatographic methods which rely on retention times for compound identification, the qualitative reliability is not as good as that of methods using mass spectrometry or infrared analysis for the characterization of each peak.

Because of the complexity of most aircraft fuels, no method using GC alone, even using high resolution capillary columns, can provide maximum compound resolution. As shown by the studies combining HPLC with GC-MS for the determination of nitrogen-containing compounds, a method combining high resolution GC with high resolution LC is necessary for obtaining maximum resolution.

The GC-UVD has a linear range of about 1000. A linear range of 10^4 is desirable. In practice a linear range of 10^4, at levels of 0.2 to 2000 ng, can only be achieved with a flame detector, e.g., FID or AFD. However, when a capillary column is used to achieve high resolution, the upper end of the range often can not be used because of column overloading problems. The limitation in the GC-UVD range is mainly a problem for the analysis of fuels having high contents of naphthalenes. Because of the lower extinction coefficients of benzenes, high levels of benzenes do not usually saturate the detector.

2. GC-PID

The use of a photoionization detector using a 9.5-e.v. source for GC analysis has many of the same performance features of GC-UVD. GC-PID is more sensitive than GC-UVD but is not as good in terms of selectivity and quantitative reliability.

3. GC-AFD

The use of rubidium-bead alkali flame detector for GC analysis is an excellent approach to the determination of nitrogen-containing compounds, however, the method is not suitable for the determination of aromatic hydrocarbons.

4. GC-FID

Although GC-FID is commonly used for the analysis of fuels, it has no selectivity. Therefore, GC-FID is more subject to interference from unresolved components than are methods that use selective detectors.

5. LC + GC-PID

By combining liquid chromatography (LC), specifically fractionation using a silica gel column, with GC-PID, the saturated hydrocarbons are removed from the aromatic fraction and the poor selectivity of the PID is no longer a problem. However, there would still be a deficiency in quantitative reliability and the linear range. Also the addition of a second step would sacrifice speed, simplicity, and cost to some extent.

6. LC + GC-FID

The combination of LC with GC-FID for the determination of aromatic hydrocarbons is an excellent method. It has many of the good performance qualities of GC-UVD and also has a greater linear range. However, since it is a two-step method, some sacrifice in speed, simplicity, and cost must be accepted.

7. LC + GC-IR

The main advantage of LC combined with GC-IR (using Fourier-Transform, (FT) instrumentation) is the additional qualitative reliability achieved. The IR

spectra can differentiate between many isomers that even GC-MS cannot differentiate. The main disadvantage is poor sensitivity; however, the sensitivity will undoubtedly improve as GC-FTIR instrumentation is improved. The GC resolution achieved using FTIR as a detector is not as good as that with other detectors. LC combined with GC-IR would be useful primarily for the identification of high level compounds whose isomeric identity cannot be determined by GC-MS. This combined method is very costly.

8. LC + GC-MS

The use of GC-MS to analyze an aromatic fraction obtained by LC has the good performance qualities of LC + GC-FID and also provides a high degree of qualitative reliability. Although GC-MS is commonly used, the method is much more costly than GC-FID.

9. HPLC-UVD

High performance liquid chromatography, using a normal phase column and an ultraviolet detector is suitable for the determination of many aromatic components in a fuel. HPLC-UVD has many of the good performance features of GC-UVD; however, it is not capable of resolving as many different compounds. For the latter reason qualitative reliability is not as good as that of GC-UVD.

10. HPLC + GC-UVD

The combination of HPLC with GC-UVD involves the collection of numerous (5 to 10) HPLC fractions and the analysis of each fraction by GC-UVD. The main advantage that the combined method offers is an ability to resolve a greater number of compounds. The method takes much longer and is much more costly than GC-UVD alone.

11. HPLC + GC-FID

The combination of HPLC with GC-FID offers the same advantages as LC + GC-FID and in addition permits a much greater number of compounds to be resolved and quantified. The method takes longer and is more costly than LC + GC-FID.

12. HPLC + GC-IR

The combination of HPLC with GC-IR offers the same advantages of LC + GC-IR and in addition permits a much greater number of compounds to be resolved and characterized. The poor sensitivity of GC-IR would remain a problem. Because of the inferior GC resolution currently achieved with GC-IR, the use of HPLC instead of LC combined with GC-IR offers a very significant advantage. The combined method would take a lot of time and be very costly.

13. HPLC + GC-MS

The combination of HPLC with GC-MS will provide the greatest amount of information for any one of the methods discussed. This combined method has the same advantages of LC + GC-MS and in addition permits a much greater number of compounds to be resolved and characterized. The method is very time consuming and costly.

C. RECOMMENDED ANALYTICAL SCHEMES

1. Routine Analyses

For the routine analysis of aircraft fuels we recommend the simultaneous use of GC-UVD, GC-AFD, and GC-FID. The effluent from a high resolution fused silica capillary column would be passed through a

UVD. The effluent from the UVD would go to a tee with makeup gas introduced and split 1:1 to an FID and AFD. With this analysis scheme, the selectivity of the UVD is used for the determination of the aromatic components, the selectivity of the AFD is used for the determination of nitrogen-containing compounds, and the FID is used for the quantification of major amounts of normal paraffins and major amounts of aromatics, especially naphthalenes, that may saturate the UVD. Since only a single GC run is involved, a maximum amount of information is obtained in a minimum amount of time and at a minimal cost.

Calibration mixtures containing a wide variety of reference compounds of interest and run at five or more concentration levels should be interspersed with the fuel samples. The analysis of one calibration sample for every four fuel samples is recommended. The use of a good computer system is recommended to calculate response factors and process the large volume of data generated.

The injection of the samples as the neat fuels is recommended. This injection procedure permits all components, including the lower-boiling components, to be detected by the FID; however, the high split ratio required may make the quantification somewhat less reliable. The injection of neat fuels requires calibration mixtures to be prepared in a nonaromatic naphtha, preferably one with no significant amounts of normal paraffins. Internal standards, one for use with each detector, need to be mixed into each fuel sample. p-Fluorotoluene, at a level of 2.0 g/100 g, is recommended as the internal standard for use with the UVD. Compounds such as 2-fluoropyridine and decylcyclohexane may be suitable as internal standards for use with the AFD and FID, respectively.

The injection of samples in hexane or pentane solution can also be used. Splitless or on-column injection can be used for the injection of solutions which may give slightly better quantitative reliability but less sensitivity. Also, low-boiling components, e.g., cyclohexane and benzene, cannot be detected by the FID when solutions are used because the lower-boiling components are obsured by the solvent peak.

2. Confirmatory Analyses

In order to confirm the identity of most of the aromatic components being detected by GC-UVD, we recommend the use of LC + GC-MS. The LC fractionation is relatively simple to perform. The GC-MS data will usually permit the molecular formula of a component to be determined and frequently the fragmentation pattern will permit a particular isomer to be identified. We recommend the use of both the EI and CI modes. The EI data provide characteristic fragmentation patterns and reliable molecular weights can be determined from the CI data.

We recommend that a confirmatory analysis be performed on each sample that gives a GC pattern that is very significantly different from that of any other fuels for which confirmatory analyses have been run.

For the confirmation of the identity of nitrogen-containing compounds detected by the AFD, a basic fraction, obtained by acid-base extraction, should be analyzed by GC-MS.

3. Detailed Analyses

For a highly detailed analysis of a fuel sample, we recommend the use of HPLC combined with both GC-MS and GC-IR. At least five HPLC fractions and up to about 20 fractions would each be analyzed individually. The GC-IR data would supplement the GC-MS data and assist in the identification of specific isomers. The GC-MS analyses should be run in both the EI and CI modes.

This detailed analysis approach would be very time consuming and costly. The analyses could be simplified by omitting the GC-IR analyses. The instrumentation currently available for capillary column GC-IR is only capable of detecting relatively high concentrations. The HPLC fractions would undoubtedly need to be concentrated in most cases 100-fold or more. Although some of the lower-boiling components would be lost, those components are readily resolved and identified without the use of HPLC.

We recommend that a detailed analysis be performed on only a few fuel samples which are of greatest interest or which are representative of the greatest number of different samples.

REFERENCES

1. W. Kaye, Anal. Chem., 34, 287 (1963).

   A far-ultraviolet spectrophotometer operated at a wavelength of 165 to 220 nm was used as a GC detector by using a 1-cm flow-through cell that had a volume of 1.5 ml.

2. J. Merritt, F. Comendant, S. T. Abrams, and V. N. Smith, Anal. Chem., 35, 1461 (1963).

   An ultraviolet analyzer using radiation from a low-pressure mercury vapor lamp, 254 nm, and using an 8-cm flow-through cell with a volume of 7 ml was used as a GC detector to determine aromatic hydrocarbons in process streams.

3. M. Inoue and D. Ishii, Kogyo Kagaku Zasshi, 74, 2045 (1971) (Japanese).

   Continuous GC-UV and GC-IR was applied to xylene.

4. J. W. Robinson and J. P. Goodbread, Anal. Chim. Act., 66, 239 (1973).

   A vapor-phase fluorescence detector having a cell volume of 116 ml was developed for the GC analysis of polynuclear aromatic compounds.

5. T. Tsuda and D. Ishii, Bunseki Kiki, 11, 511 (1973) (Japanese). C.A., 80, 78133s (1974).

   GC-UV and GC-IR are reviewed.

6. T. Tsuda and D. Ishii, J. Chromatog., 96, 171 (1974).

   A GC-UV detector is described in which ethanol vapor is mixed with the GC effluent, then condensed and passed into a cell used for LC-UV.

7. D. Ishii, Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku, 25, 333 (1974) (Japanese). C.A., 84, 25352p (1976).

   GC-UV was accomplished by mixing the GC effluent with ethanol vapor followed by condensation and use of a liquid cell.

8. R. A. Greinke and I. C. Lewis, Prepr., Div. Pet. Chem., Am. Chem. Soc., 20, 787 (1975).

   A GC-UV method involving trapping of GC peaks followed by UV analysis was used to monitor petroleum pitch volatiles.

9. R. D. Butler, Technical Memorandum No. AFAPL-SFF-TM-74-20, November, 1974.

Design criteria are presented for the development of an ultraviolet detector for the selective GC analysis of aromatic hydrocarbons in jet fuels.

10. P. M. Houpt and G. H. W. Baalhuis, Appl. Spectrosc., 31, 473 (1977).

A second derivative UV spectrophotometer is described which used a 3-ml cell with a 1-meter path length and which can be used with a GC.

11. F. N. Hodgson, H. C. Tucker, and R. D. Butler, Report No. AFAPL-TR-77-60, Interim Technical Report from Monsanto Research Corp., November, 1977.

12. A. A. Grinberg, T. Y. Bigdash and S. V. Leontiva, Fiz.-khim Metody Issled. Nefteproduktov, M., 23, (1979) (Russian). C.A. 93, 75273v (1980).

An ultraviolet detector operated at 254 nm was used as a selective detector for the capillary column GC analysis of naphthalenes in jet fuels.

13. T. D. Searl, W. K. Robbins and R. A. Brown, ASTM Spec. Tech. Publ. STP 686, p. 164-80 (1979).

A GC-UV method is described for the determination of polynuclear aromatic hydrocarbons. The method involves the collection of GC fractions and the determination of their UV absorption spectra.

14. W. K. Robbins, T. D. Searl, D. H. Wasserstrom and G. T. Boyer, ASTM Spec. Tech. Publ. STP 720, p. 149-66 (1980).

A GC-UV method is described for the determination of polynuclear aromatic hydrocarbons. The method involves the collection of GC fractions and the determination of their UV absorption spectra.

15. M. Novotny, F. J. Schwende, M. J. Hartigan and J. E. Purcell, Anal. Chem., 52, 736 (1980).

The use of the Perkin-Elmer GC-55 UV detector is described for the detection of UV-absorbing compounds in gasoline, volatiles of physiological fluids, and mixtures of polynuclear aromatic hydrocarbons.

16. F. J. Schwende, M. Novotny and J. E. Purcell, Chromatogr. Newsl., 8, 1 (1980).

The use of the Perkin-Elmer GC-55 UV detector is described for the detection of aromatic hydrocarbons in gasoline using a setting of 260 nm and polynuclear aromatic compounds in coal tar using a setting of 250 nm.

17. A. Karmen, T. Pritchett and S. Lam, J. Chromatog., 217, 247 (1981).

Therapeutic drugs were determined by a GC-UV method in which the GC effluent was scrubbed into a stream of 2-propanol which was drawn through a 20-µl UV detector flow cell.

APPENDIX A

METHOD FOR SEPARATION OF AROMATICS AND NONAROMATICS IN AIRCRAFT FUELS

APPENDIX A

METHOD FOR SEPARATION OF AROMATICS AND NONAROMATICS IN AIRCRAFT FUELS

A. SCOPE AND APPLICATION

1. This method covers the separation of aromatics from nonaromatics in gasoline, fuel oils, and crude oils.
2. Pentane-insoluble components are removed by centrifugation prior to the separation.
3. The separated aromatic and nonaromatic fractions obtained can be used directly without concentration for GC analysis of all components that boil above 75°C.

B. SUMMARY

The sample dissolved in n-pentane is introduced to a glass chromatographic column packed with activated silica gel. The nonaromatics are eluted first with n-pentane and the aromatics are eluted second with methylene chloride.

C. DEFINITIONS

1. Nonaromatics are comprised of the paraffinic, naphthenic and olefinic hydrocarbons.
2. Aromatics are comprised of aromatic hydrocarbons, condensed naphthenic aromatic hydrocarbons, aromatic olefins, and some of the less polar heterocyclic compounds such as benzothiophenes and carbazoles.

D. APPARATUS AND REAGENTS

1. Chromatographic Column, 250 mm x 9 mm O.D. glass column fitted with a sintered glass disc and Teflon stopcock at the bottom.
2. Centrifuge, capable of handling standard 15-ml centrifuge tubes at 3000 RPM.
3. Centrifuge tubes, 15-ml, glass, calibrated, conical type.
4. Syringe, 250-µl.
5. Syringe, 2 ml.

6. Graduated Cylinder, 100-ml.
7. Collection bottles, 30-ml, narrow-mouth, glass, with Teflon-lined screw cap.
8. Beaker, 100-ml.
9. Silica gel, 100-200 mesh, Davison Grade 923, activated in an open container in an oven at 150°C for at least 16 hours but no more than 80 hours.
10. Methylene Chloride, Burdick and Jackson distilled-in-glass grade or equivalent.
11. Pentane, Burdick and Jackson distilled-in-glass grade or equivalent.

E. PROCEDURE

1. Suspend 10 g of silica gel in 20 ml of methylene chloride in a 100-ml beaker.

2. Pour the slurry into the chromatographic column with the stopcock open.

3. Wash the remaining silica gel onto the column with another 20 ml of methylene chloride. Allow the liquid level to move down nearly to the top of the silica gel (within 1 mm) and close the stopcock.

4. Rinse the top of the column with 2 ml of pentane and open the stopcock to again allow the liquid level to move down nearly to the top of the silica gel. Make sure the solvent level in the column never goes below the silica gel level during the entire silica gel procedure. Repeat this rinse step using 2 ml and again using 35 ml of pentane.

5. Add 250 µl of sample if nonviscous or 250 mg of sample if too viscous for syringe sampling to 100 ml of pentane contained in a glass stoppered centrifuge tube. Mix thoroughly by repeated inversions. If insoluble material is present, centrifuge for 15 minutes at approximately 3000 RPM.

6. Apply 2.0 ml of the pentane solution of the sample, using a syringe, to the top of the chromatographic column and allow the liquid level to move down nearly to the top of the silica gel.

7. Fill the syringe with 2 ml of pentane, apply this solvent to the column, and again allow the liquid level to move down nearly to the top of the silica gel. Repeat this step once more. Discard all eluates up to this point.

8. Elute with 20 ml of pentane followed by 30 ml of methylene chloride.

9. Collect two 25-ml eluate fractions. The first fraction contains the nonaromatics and the second fraction contains the aromatics.

APPENDIX B

UVD CELL ASSEMBLY AND ALIGNMENT

APPENDIX B

UVD CELL ASSEMBLY AND ALIGNMENT

A. CELL ASSEMBLY

1. Insert a fused silica column and fused silica exit tubing (0.61 mm O.D.) into the transfer line casing.

2. Apply Silastic 734 TRV adhesive (Dow Corning) to the outside end of the drilled holes (0.65 mm I.D.) of the cell body.

3. Insert the column through the adhesive into the hole. Make sure that the adhesive gets into the hole by pushing and pulling on the column until the drilled hole is full of adhesive. Repeat this step for the exit tubing.

4. Push the column and exit tubing through the drilled holes until it touches the inside wall.

5. Tape down the cell body so that there is no pressure on the column or exit tubing.

6. Allow the adhesive to cure overnight at room temperature.

7. Twist a No. 65 drill bit into each end of the cell body to cut off the excess of the fused silica capillaries.

8. Place the cell body into one half of the cell holder. Place the other half of the cell holder on top and bolt together.

9. Carefully place the cell holder in a vertical position. Insert into the one end

A. 6-ml silicone gasket
B. cell window
C. 1/16-in. silicone gasket
D. spacer
E. end plate with the two long bolts inserted into the cell holder

10. Turn the cell holder so that the other end is up. Make sure that the spacer, window and gaskets do not fall out.

11. Repeat step 9.

12. Tighten the nuts on the two long bolts. Look down the light path to see if the gaskets are blocking the light path. If any portion of the light path is blocked, disassemble the cell window and start at Step 9 again.

13. Attach the bottom plate to the cell holder.

14. Plug in the transfer line heater and thermocouple.

15. Insert the cartridge heater and thermocouple into the cell holder.

16. Bolt the cell holder bottom plate to the standoffs.

B. CELL ALIGNMENT

1. Make sure detector shutter is closed.

2. Turn on UV detector.

3. Select the tungsten lamp and turn it on.

4. Set wavelength to 0.

5. Align the cell holder so that the light beam is centered on the entrance to the cell. This is done by loosening the two bolts that attach the

bottom plate of the cell to the standoffs and moving the cell holder until the light beam is centered.

6. Adjust the cell holder so that the maximum light intensity exits the cell. This is done in the same manner as the entrance alignment. Make sure that the entrance alignment is not changed.

7. Change the lamp switch to UV. Turn on UV lamp power supply.

8. Set the wavelength to 208 nm.

9. Cover the cell compartment with an opaque cloth to block out light.

10. Open the detector shutter and move the cell holder very slightly back and forth to get the largest negative number on the digital readout of the spectrophotometer. Do not move the cell holder very much; this is just a fine adjustment.

11. Close the detector shutter and remove the cloth.

12. Tighten the bolts that attach the bottom plate of the cell holder to the standoffs.

13. Place the insulation around cell holder taking care to keep the cell windows clean. Close cover.

14. Turn on detector and transfer line heaters.

APPENDIX C

ANALYTICAL DATA FROM THE ANALYSIS OF AIRCRAFT FUELS

TABLE C-1. AROMATIC HYDROCARBON COMPOSITION OF FUEL SAMPLES DETERMINED BY GC-UVD ANALYSIS OF HEXANE SOLUTIONS, SET A

GC Peak No.[a]	Amount Found,[b] g/100g, in Given Sample				
	VN-80-39	VN-80-40	VN-80-41	VN-80-47	VN-80-48
1	<0.1	<0.1	1.08 ± 0.02	<0.1	0.64 ± 0.03
2	0.44 ± 0.01	<0.1	0.24 ± 0.02	<0.1	0.14 ± 0.01
3	3.10 ± 0.08	<0.1	1.02 ± 0.06	<0.1	0.58 ± 0.10
4	3.00 ± 0.22	<0.1	0.40 ± 0.02	<0.1	0.26 ± 0.02
5	5.88 ± 0.25	<0.1	0.12 ± 0.08	<0.1	<0.1
6	4.98 ± 0.21	0.08 ± 0.06	0.15 ± 0.08	<0.1	0.09 ± 0.01
7	17.03 ± 0.96	0.36 ± 0.02	0.57 ± 0.08	0.09 ± 0.03	0.44 ± 0.03
8	8.52 ± 0.40	0.34 ± 0.05	0.40 ± 0.07	0.10 ± 0.01	0.37 ± 0.04
9	6.48 ± 0.41	0.23 ± 0.08	0.23 ± 0.04	0.11 ± 0.03	0.19 ± 0.03
10	12.46 ± 0.74	1.35 ± 0.06	0.92 ± 0.09	0.42 ± 0.02	1.08 ± 0.11
13	1.90 ± 0.70	0.54 ± 0.01	0.33 ± 0.05	0.19 ± 0.02	0.42 ± 0.05
15	<0.1	<0.1	<0.1	<0.1	<0.1
16	<0.1	0.25 ± 0.01	<0.1	<0.1	<0.1
17	0.44 ± 0.01	0.55 ± 0.05	0.23 ± 0.04	0.18 ± 0.04	0.38 ± 0.09
18	<0.1	0.43 ± 0.03	<0.1	<0.1	<0.1
19	0.28 ± 0.04	0.85 ± 0.01	0.27 ± 0.06	0.23 ± 0.03	0.45 ± 0.06
20	<0.1	0.23 ± 0.03	<0.1	0.11 ± 0.01	0.32 ± 0.27
21	<0.1	0.77 ± 0.03	<0.1	0.26 ± 0.05	0.45 ± 0.08
22	<0.1	1.08 ± 0.05	0.21 ± 0.02	0.28 ± 0.01	0.56 ± 0.08
23	<0.1	<0.1	<0.1	<0.1	<0.1
24	<0.1	<0.1	<0.1	<0.1	<0.1
25	<0.1	0.30 ± 0.02	<0.1	0.17 ± 0.02	0.17 ± 0.04
27	<0.1	1.32 ± 0.08	0.23 ± 0.05	0.34 ± 0.02	0.47 ± 0.08
28	<0.1	1.57 ± 0.03	0.24 ± 0.39	0.45 ± 0.01	0.77 ± 0.06
29	<0.1	0.39 ± 0.03	<0.1	0.07 ± 0.02	0.15 ± 0.01
31	<0.1	0.80 ± 0.07	<0.1	0.19 ± 0.02	0.36 ± 0.03
32	<0.1	0.72 ± 0.01	<0.1	0.61 ± 0.03	0.38 ± 0.02
33	<0.1	<0.1	<0.1	<0.1	<0.1
34	<0.1	<0.1	<0.1	<0.1	<0.1

TABLE C-1. (Continued)

GC Peak No.[a]	Amount Found,[b] g/100g, in Given Sample				
	VN-80-39	VN-80-40	VN-80-41	VN-80-47	VN-80-48
39	<0.02	3.95 ± 0.38	0.23 ± 0.02	1.84 ± 0.07	3.16 ± 0.12
40	<0.1	<0.1	<0.1	<0.1	<0.1
42	<0.1	1.07 ± 0.03	<0.1	0.23 ± 0.08	0.40 ± 0.05
44	<0.1	0.62 ± 0.02	<0.1	0.20 ± 0.03	0.22 ± 0.07
47	<0.1	<0.1	<0.1	0.10 ± 0.04	0.16 ± 0.01
49	<0.1	1.15 ± 0.05	<0.1	0.24 ± 0.03	0.45 ± 0.03
50	<0.1	0.87 ± 0.02	<0.1	0.21 ± 0.03	0.38 ± 0.04
54	<0.02	6.40 ± 0.68	0.37 ± 0.04	3.88 ± 0.22	6.11 ± 0.11
55	<0.02	5.31 ± 0.53	0.21 ± 0.01	2.24 ± 0.11	3.91 ± 0.21
56	<0.1	<0.1	<0.1	<0.1	<0.1
62	<0.02	1.99 ± 0.12	0.04 ± 0.01	0.50 ± 0.01	0.95 ± 0.08
64	<0.02	2.50 ± 0.16	0.08 ± 0.01	0.66 ± 0.01	1.27 ± 0.11
65	<0.02	2.88 ± 0.21	0.08 ± 0.02	0.85 ± 0.02	1.56 ± 0.12
67	<0.02	2.04 ± 0.19	0.04 ± 0.02	0.52 ± 0.03	0.95 ± 0.13
69	<0.02	1.08 ± 0.06	<0.02	0.25 ± 0.01	0.47 ± 0.05
71	<0.1	0.93 ± 0.03	<0.1	0.18 ± 0.05	0.37 ± 0.05
73	<0.02	0.90 ± 0.07	<0.02	0.22 ± 0.01	0.39 ± 0.05
77	<0.02	0.51 ± 0.02	<0.02	0.13 ± 0.02	0.24 ± 0.05
78	<0.02	0.70 ± 0.03	<0.02	0.18 ± 0.01	0.33 ± 0.04
79	<0.02	0.40 ± 0.02	<0.02	0.11 ± 0.01	0.22 ± 0.08
80	<0.02	0.64 ± 0.03	<0.02	0.16 ± 0.01	0.26 ± 0.03
81	<0.02	0.48 ± 0.03	<0.02	0.13 ± 0.01	0.21 ± 0.03
82	<0.02	0.32 ± 0.04	<0.02	0.10 ± 0.03	0.13 ± 0.02
84	<0.02	0.35 ± 0.02	<0.02	0.09 ± 0.02	0.15 ± 0.02
89	<0.02	<0.02	<0.02	<0.02	<0.02
90	<0.02	0.13 ± 0.02	<0.02	<0.02	0.05 ± 0.01
91	<0.02	0.09 ± 0.01	<0.02	<0.02	<0.02
92	<0.02	0.16 ± 0.02	<0.02	<0.02	0.06 ± 0.01

(a) The tentative identifications of the GC peaks are given in Table 2.

(b) Average of three runs.

TABLE C-2. AROMATIC HYDROCARBON COMPOSITION OF FUEL SAMPLES DETERMINED BY GC-UVD ANALYSIS OF HEXANE SOLUTIONS, SET B

GC Peak No.[a]	Amount Found,[b] g/100g, in Given Sample				
	VN-80-50	VN-80-52	VN-80-56	VN-80-59	VN-80-60
1	0.54 ± 0.01	0.87 ± 0.01	<0.1	0.05 ± 0.01	<0.1
2	0.35 ± 0.01	0.23 ± 0.02	<0.1	<0.1	<0.1
3	2.21 ± 0.02	1.08 ± 0.04	< 0.1	0.13 ± 0.01	0.10 ± 0.01
4	2.03 ± 0.04	0.56 ± 0.12	<0.1	<0.1	0.06 ± 0.01
5	3.75 ± 0.10	0.67 ± 0.03	<0.1	<0.1	<0.1
6	3.10 ± 0.09	0.57 ± 0.03	< 0.1	<0.1	<0.1
7	11.95 ± 0.56	2.61 ± 0.14	< 0.1	0.13 ± 0.01	0.20 ± 0.01
8	5.34 ± 0.18	1.16 ± 0.06	<0.1	0.12 ± 0.02	0.18 ± 0.01
9	4.02 ± 0.13	0.83 ± 0.05	< 0.1	0.09 ± 0.02	0.12 ± 0.01
10	8.84 ± 0.52	2.29 ± 0.17	0.28 ± 0.02	0.26 ± 0.01	0.60 ± 0.02
13	1.19 ± 0.06	0.40 ± 0.04	0.15 ± 0.01	0.13 ± 0.03	0.23 ± 0.02
15	<0.1	<0.1	<0.1	<0.1	<0.1
16	0.32 ± 0.01	<0.1	<0.1	<0.1	<0.1
17	0.34 ± 0.01	0.27 ± 0.01	< 0.1	0.09 ± 0.01	0.22 ± 0.01
18	<0.1	<0.1	<0.1	<0.1	0.17 ± 0.01
19	0.24 ± 0.02	0.19 ± 0.03	<0.1	0.09 ± 0.01	0.32 ± 0.02
20	<0.1	<0.1	<0.1	<0.1	0.11 ± 0.01
21	0.16 ± 0.02	0.19 ± 0.03	0.12 ± 0.02	<0.1	0.30 ± 0.03
22	0.15 ± 0.03	0.19 ± 0.02	0.10 ± 0.03	<0.1	0.37 ± 0.02
23	<0.1	<0.1	<0.1	<0.1	<0.1
24	<0.1	<0.1	< 0.1	<0.1	<0.1
25	<0.1	0.10 ± 0.03	0.13 ± 0.02	<0.1	0.15 ± 0.01
27	<0.1	<0.1	< 0.1	<0.1	0.44 ± 0.02
28	<0.1	0.11 ± 0.04	0.25 ± 0.02	< 0.1	0.51 ± 0.02
29	<0.1	<0.1	< 0.1	<0.1	0.12 ± 0.01
31	<0.1	<0.1	<0.1	<0.1	0.27 ± 0.03
32	<0.1	0.12 ± 0.04	0.50 ± 0.05	< 0.1	0.26 ± 0.02
33	<0.1	<0.1	<0.1	< 0.1	<0.1
34	<0.1	<0.1	<0.1	<0.1	<0.1

TABLE C-2. (Continued)

GC Peak No.[a]	Amount Found,[b] g/100g, in Given Sample				
	VN-80-50	VN-80-52	VN-80-56	VN-80-59	VN-80-60
39	0.11 ± 0.01	0.19 ± 0.02	0.25 ± 0.01	0.22 ± 0.01	2.35 ± 0.03
40	<0.1	<0.1	<0.1	<0.1	<0.1
42	<0.1	<0.1	<0.1	<0.1	0.26 ± 0.08
44	<0.1	<0.1	<0.1	<0.1	0.20 ± 0.03
47	<0.1	<0.1	0.21 ± 0.05	<0.1	0.16 ± 0.01
49	<0.1	<0.1	<0.1	<0.1	0.31 ± 0.01
50	<0.1	<0.1	<0.1	<0.1	0.25 ± 0.04
54	0.16 ± 0.01	0.29 ± 0.02	0.53 ± 0.03	0.73 ± 0.03	4.70 ± 0.01
55	0.08 ± 0.01	0.15 ± 0.02	0.37 ± 0.01	0.46 ± 0.01	2.94 ± 0.73
56	<0.1	<0.1	<0.1	<0.1	<0.1
62	0.02 ± 0.01	0.04 ± 0.01	0.09 ± 0.01	0.18 ± 0.01	0.75 ± 0.03
64	0.04 ± 0.01	0.07 ± 0.01	0.13 ± 0.01	0.33 ± 0.01	1.06 ± 0.04
65	0.03 ± 0.01	0.08 ± 0.01	0.18 ± 0.01	0.38 ± 0.02	1.28 ± 0.04
67	0.02 ± 0.01	0.04 ± 0.01	0.10 ± 0.01	0.22 ± 0.01	0.78 ± 0.06
69	<0.02	<0.02	<0.02	0.11 ± 0.01	0.39 ± 0.03
71	<0.1	<0.1	<0.1	0.34 ± 0.05	0.39 ± 0.05
73	<0.02	<0.02	<0.02	0.17 ± 0.01	0.39 ± 0.04
77	<0.02	<0.02	<0.02	0.12 ± 0.01	0.23 ± 0.02
78	<0.02	<0.02	<0.02	0.19 ± 0.01	0.34 ± 0.02
79	<0.02	<0.02	<0.02	0.12 ± 0.01	0.19 ± 0.02
80	<0.02	<0.02	<0.02	0.15 ± 0.01	0.29 ± 0.02
81	<0.02	<0.02	<0.02	0.14 ± 0.01	0.23 ± 0.02
82	<0.02	<0.02	<0.02	0.11 ± 0.02	0.16 ± 0.05
84	<0.02	<0.02	<0.02	0.10 ± 0.04	0.16 ± 0.05
89	<0.02	<0.02	<0.02	0.08 ± 0.03	0.07 ± 0.02
90	<0.02	<0.02	<0.02	<0.02	0.07 ± 0.02
91	<0.02	<0.02	<0.02	<0.02	0.06 ± 0.02
92	<0.02	<0.02	<0.02	<0.02	0.10 ± 0.03

(a) The tentative identification of the GC peaks are given in Table 2.

(b) Average of three runs.

TABLE C-3. AROMATIC HYDROCARBON COMPOSITION OF FUEL SAMPLES DETERMINED BY GC-UVD ANALYSIS OF HEXANE SOLUTIONS, SET C

GC Peak No.[a]	Amount Found,[b] g/100g, in Given Sample				
	VN-80-61	VN-80-62	VN-80-67	VN-80-68	VN-80-69
1	1.03 ± 0.01	<0.1	0.53 ± 0.01	0.92 ± 0.01	<0.1
2	0.15 ± 0.01	<0.1	0.11 ± 0.01	0.25 ± 0.01	<0.1
3	0.86 ± 0.03	<0.1	0.71 ± 0.01	0.89 ± 0.02	0.11 ± 0.01
4	0.33 ± 0.01	<0.1	0.27 ± 0.01	0.43 ± 0.01	0.06 ± 0.01
5	<0.1	<0.1	<0.1	<0.1	<0.1
6	0.11 ± 0.04	0.08 ± 0.01	0.07 ± 0.01	0.14 ± 0.01	<0.1
7	0.35 ± 0.01	0.33 ± 0.01	0.28 ± 0.01	0.57 ± 0.03	0.12 ± 0.01
8	0.25 ± 0.01	0.28 ± 0.02	0.23 ± 0.04	0.40 ± 0.03	0.13 ± 0.02
9	0.14 ± 0.04	0.30 ± 0.03	0.12 ± 0.02	0.33 ± 0.04	0.11 ± 0.02
10	0.56 ± 0.04	1.04 ± 0.03	0.48 ± 0.01	1.03 ± 0.01	0.33 ± 0.02
13	0.26 ± 0.01	0.95 ± 0.03	0.18 ± 0.01	0.44 ± 0.02	0.17 ± 0.03
15	<0.1	0.21 ± 0.02	<0.1	<0.1	<0.1
16	<0.1	0.30 ± 0.02	<0.1	<0.1	<0.1
17	0.16 ± 0.01	0.41 ± 0.02	0.14 ± 0.02	0.19 ± 0.01	0.16 ± 0.03
18	<0.1	0.37 ± 0.01	0.12 ± 0.01	0.16 ± 0.01	0.14 ± 0.04
19	<0.1	0.35 ± 0.01	0.12 ± 0.02	0.20 ± 0.02	0.23 ± 0.03
20	<0.1	0.25 ± 0.01	<0.1	0.16 ± 0.02	0.15 ± 0.01
21	<0.1	0.48 ± 0.02	<0.1	0.24 ± 0.03	0.30 ± 0.01
22	<0.1	0.38 ± 0.01	0.13 ± 0.01	0.19 ± 0.04	0.22 ± 0.02
23	<0.1	0.18 ± 0.02	<0.1	<0.1	<0.1
24	<0.1	0.43 ± 0.02	0.14 ± 0.02	0.13 ± 0.02	0.25 ± 0.01
25	<0.1	<0.1	<0.1	<0.1	<0.1
27	<0.1	0.32 ± 0.04	0.10 ± 0.01	0.20 ± 0.04	0.30 ± 0.01
28	<0.1	0.30 ± 0.04	<0.1	<0.1	0.34 ± 0.02
29	<0.1	<0.1	<0.1	<0.1	<0.1
31	<0.1	0.39 ± 0.05	0.13 ± 0.02	<0.1	<0.1
32	<0.1	<0.1	<0.1	<0.1	<0.1
33	<0.1	0.23 ± 0.05	<0.1	0.16 ± 0.03	0.30 ± 0.03
34	<0.1	0.44 ± 0.07	<0.1	<0.1	<0.1

TABLE C-3. (Continued)

GC Peak No.[a]	Amount Found,[b] g/100g, in Given Sample				
	VN-80-61	VN-80-62	VN-80-67	VN-80-68	VN-80-69
39	0.05 ± 0.01	0.20 ± 0.01	0.02 ± 0.02	0.14 ± 0.01	0.46 ± 0.03
40	<0.1	0.41 ± 0.04	0.17 ± 0.07	<0.1	<0.1
42	0.17 ± 0.06	0.33 ± 0.03	0.14 ± 0.07	<0.1	<0.1
44	0.12 ± 0.02	0.23 ± 0.03	<0.1	<0.1	<0.1
47	<0.1	<0.1	<0.1	<0.1	<0.1
49	<0.1	<0.1	<0.1	<0.1	<0.1
50	0.19 ± 0.06	0.03 ± 0.03	0.14 ± 0.16	<0.1	<0.1
54	0.09 ± 0.03	0.26 ± 0.02	0.03 ± 0.01	0.15 ± 0.01	0.75 ± 0.06
55	0.03 ± 0.02	0.12 ± 0.02	<0.02	0.10 ± 0.01	0.48 ± 0.04
56	<0.1	<0.1	<0.1	<0.1	<0.1
62	<0.02	0.03 ± 0.01	<0.02	0.03 ± 0.01	0.13 ± 0.01
64	<0.02	0.05 ± 0.01	<0.02	0.03 ± 0.01	0.23 ± 0.02
65	<0.02	0.07 ± 0.1	<0.02	0.04 ± 0.01	0.26 ± 0.02
67	<0.02	<0.02	<0.02	<0.02	0.15 ± 0.01
69	<0.02	<0.02	<0.02	<0.02	<0.02
71	<0.1	<0.1	<0.1	<0.1	<0.1
73	<0.02	<0.02	<0.02	<0.02	<0.02
77	<0.02	<0.02	<0.02	<0.02	<0.02
78	<0.02	<0.02	<0.02	<0.02	<0.02
79	<0.02	<0.02	<0.02	<0.02	<0.02
80	<0.02	<0.02	<0.02	<0.02	<0.02
81	<0.02	<0.02	<0.02	<0.02	<0.02
82	<0.02	<0.02	<0.02	<0.02	<0.02
84	<0.02	<0.02	<0.02	<0.02	<0.02
89	<0.02	<0.02	<0.02	<0.02	<0.02
90	<0.02	<0.02	<0.02	<0.02	<0.02
91	<0.02	<0.02	<0.02	<0.02	<0.02
92	<0.02	<0.02	<0.02	<0.02	<0.02

(a) The tentative identifications of the GC peaks are given in Table 2.

(b) Average of three runs.

TABLE C-4. AROMATIC HYDROCARBON COMPOSITION OF FUEL SAMPLES DETERMINED BY GC-UVD ANALYSIS OF HEXANE SOLUTIONS, SET D

GC Peak No.(a)	VN-80-70	VN-80-71	VN-80-72	VN-80-73	VN-80-74
1	<0.1	2.38 ± 0.01	0.24 ± 0.01	1.20 ± 0.01	0.72 ± 0.01
2	<0.1	2.65 ± 0.03	<0.1	0.29 ± 0.03	0.68 ± 0.01
3	0.11 ± 0.01	8.70 ± 0.08	<0.1	4.74 ± 0.09	2.61 ± 0.03
4	0.05 ± 0.01	3.66 ± 0.04	<0.1	1 80 ± 0.04	0.97 ± 0.01
5	<0.1	0.11 ± 0.01	<0.1	<0.1	<0.1
6	<0.1	0.39 ± 0.01	<0.1	0.20 ± 0.01	0.11 ± 0.01
7	0.12 ± 0.02	2.87 ± 0.07	0.08 ± 0.03	1.44 ± 0.03	0.81 ± 0.02
8	0.14 ± 0.01	2.29 ± 0.03	0.13 ± 0.02	1.14 ± 0.02	0.66 ± 0.01
9	0.07 ± 0.01	1.04 ± 0.01	0.08 ± 0.02	0.53 ± 0.01	0.31 ± 0.01
10	0.34 ± 0.02	5.70 ± 0.11	0.36 ± 0.03	3.15 ± 0.09	1.87 ± 0.03
13	0.16 ± 0.01	1.41 ± 0.04	0.16 ± 0.01	0.76 ± 0.02	0.48 ± 0.02
15	<0.1	<0.1	<0.1	<0.1	<0.1
16	<0.1	<0.1	<0.1	<0.1	<0.1
17	0.16 ± 0.02	0.17 ± 0.01	<0.10 ± 0.01	0.16 ± 0.02	0.15 ± 0.01
18	<0.1	<0.1	<0.1	<0.1	<0.1
19	0.18 ± 0.02	0.28 ± 0.01	0.13 ± 0.01	0.22 ± 0.02	0.18 ± 0.01
20	0.13 ± 0.04	<0.1	0.07 ± 0.03	<0.1	<0.1
21	0.20 ± 0.02	0.23 ± 0.01	0.10 ± 0.02	0.19 ± 0.01	0.16 ± 0.02
22	0.15 ± 0.04	0.30 ± 0.01	0.13 ± 0.02	0.22 ± 0.01	0.18 ± 0.02
23	<0.1	<0.1	<0.1	<0.1	<0.1
24	<0.1	<0.1	<0.1	<0.1	<0.1
25	0.17 ± 0.02	<0.1	0.11 ± 0.01	<0.1	0.11 ± 0.01
27	<0.1	0.30 ± 0.02	0.17 ± 0.02	0.23 ± 0.02	0.21 ± 0.02
28	0.25 ± 0.02	0.32 ± 0.02	0.19 ± 0.02	0.26 ± 0.02	0.24 ± 0.01
29	<0.1	<0.1	<0.1	<0.1	<0.1
31	<0.1	<0.1	<0.1	<0.1	<0.1
32	0.27 ± 0.03	<0.1	0.17 ± 0.01	<0.1	<0.1
33	<0.1	<0.1	<0.1	<0.1	<0.1
34	<0.1	<0.1	<0.1	<0.1	<0.1

TABLE C-4. (Continued)

GC Peak No.(a)	Amount Found,(b) g/100g, in Given Sample				
	VN-80-70	VN-80-71	VN-80-72	VN-80-73	VN-80-74
39	0.37 ± 0.02	0.20 ± 0.01	0.21 ± 0.01	0.23 ± 0.01	0.22 ± 0.01
40	<0.1	<0.1	<0.1	<0.1	<0.1
42	<0.1	<0.1	<0.1	<0.1	<0.1
44	<0.1	<0.1	0.17 ± 0.02	<0.1	0.15 ± 0.04
47	<0.1	<0.1	<0.1	<0.1	<0.1
49	<0.1	<0.1	0.10 ± 0.01	<0.1	<0.1
50	<0.1	0.20 ± 0.02	0.31 ± 0.01	0.30 ± 0.03	0.32 ± 0.01
54	0.62 ± 0.04	1.25 ± 0.04	1.07 ± 0.03	1.26 ± 0.04	1.19 ± 0.03
55	0.37 ± 0.02	0.69 ± 0.03	0.59 ± 0.01	0.69 ± 0.01	0.66 ± 0.02
56	<0.1	0.53 ± 0.02	0.19 ± 0.01	<0.1	<0.1
62	0.10 ± 0.01	0.94 ± 0.04	0.31 ± 0.01	0.45 ± 0.02	0.69 ± 0.01
64	0.20 ± 0.01	1.07 ± 0.04	0.58 ± 0.01	0.79 ± 0.03	0.69 ± 0.01
65	0.24 ± 0.02	<0.02	0.64 ± 0.01	0.91 ± 0.03	0.79 ± 0.01
67	0.15 ± 0.01	0.57 ± 0.02	0.31 ± 0.02	0.47 ± 0.02	0.41 ± 0.01
69	0.05 ± 0.01	0.31 ± 0.02	0.17 ± 0.01	0.25 ± 0.01	0.22 ± 0.01
71	0.12 ± 0.01	0.46 ± 0.02	0.25 ± 0.01	0.38 ± 0.02	0.33 ± 0.02
73	0.07 ± 0.01	0.56 ± 0.01	0.32 ± 0.02	0.46 ± 0.02	0.40 ± 0.01
77	0.05 ± 0.01	0.33 ± 0.01	0.20 ± 0.01	0.28 ± 0.02	0.24 ± 0.01
78	0.07 ± 0.01	0.46 ± 0.02	0.26 ± 0.01	0.38 ± 0.03	0.34 ± 0.01
79	0.05 ± 0.01	0.24 ± 0.03	0.14 ± 0.01	0.21 ± 0.01	0.19 ± 0.01
80	0.05 ± 0.01	0.41 ± 0.01	0.23 ± 0.01	0.33 ± 0.01	0.30 ± 0.01
81	0.04 ± 0.01	0.33 ± 0.02	0.20 ± 0.01	0.28 ± 0.01	0.25 ± 0.01
82	<0.02	0.19 ± 0.03	0.14 ± 0.01	0.18 ± 0.02	0.18 ± 0.01
84	<0.02	0.24 ± 0.05	0.18 ± 0.01	0.10 ± 0.01	0.22 ± 0.01
89	<0.02	0.14 ± 0.03	0.09 ± 0.01	0.12 ± 0.01	0.12 ± 0.01
90	<0.02	0.13 ± 0.02	0.08 ± 0.01	0.12 ± 0.01	0.11 ± 0.01
91	<0.02	0.11 ± 0.01	0.06 ± 0.01	0.10 ± 0.01	0.09 ± 0.01
92	<0.02	0.16 ± 0.06	0.12 ± 0.01	0.17 ± 0.01	0.15 ± 0.01

(a) The tentative identifications of the GC peaks are given in Table 2.

(b) Average of three runs.

TABLE C-5. AROMATIC HYDROCARBON COMPOSITION OF FUEL SAMPLES DETERMINED BY GC-UVD ANALYSIS OF NEAT SAMPLES, SET E

GC Peak No.[a]	Amount Found,[b] g/100 g, in Given Sample			
	VN-80-40	VN-80-41	VN-80-48	VN-80-50
0	<0.01	0.565 ± 0.013	0.345 ± 0.004	0.267 ± 0.004
1	0.026 ± 0.001	1.46 ± 0.01	0.904 ± 0.001	0.714 ± 0.004
2	<0.01	0.387 ± 0.004	0.252 ± 0.031	0.533 ± 0.013
3	<0.01	1.46 ± 0.02	0.869 ± 0.030	2.59 ± 0.04
4	<0.01	0.679 ± 0.001	0.416 ± 0.006	2.47 ± 0.03
5	<0.01	0.093 ± 0.003	0.063 ± 0.002	3.29 ± 0.06
6	0.083 ± 0.003	0.162 ± 0.001	0.126 ± 0.002	2.60 ± 0.05
7	0.379 ± 0.006	0.566 ± 0.012	0.470 ± 0.010	5.56 ± 0.19[c]
8	0.346 ± 0.005	0.397 ± 0.003	0.361 ± 0.007	3.49 ± 0.08
9	0.232 ± 0.002	0.267 ± 0.003	0.244 ± 0.004	3.14 ± 0.06
10	1.46 ± 0.04	1.11 ± 0.03	1.23 ± 0.01	4.75 ± 0.06
13	0.678 ± 0.007	0.412 ± 0.022	0.494 ± 0.012	1.36 ± 0.04
15	<0.01	<0.1	<0.1	0.321 ± 0.009
16	0.348 ± 0.004	0.110 ± 0.002	0.198 ± 0.004	0.440 ± 0.032
17	0.634 ± 0.012	0.257 ± 0.001	0.407 ± 0.008	0.439 ± 0.034
18	0.526 ± 0.003	0.194 ± 0.002	0.321 ± 0.007	0.283 ± 0.021
19	0.940 ± 0.030	0.285 ± 0.013	0.556 ± 0.013	0.331 ± 0.033
20	0.317 ± 0.009	0.147 ± 0.004	0.207 ± 0.008	0.149 ± 0.008
21	0.915 ± 0.032	0.227 ± 0.011	0.559 ± 0.022	0.218 ± 0.003
22	1.21 ± 0.04	0.264 ± 0.005	0.664 ± 0.021	0.202 ± 0.012
25	0.364 ± 0.021	0.126 ± 0.007	0.221 ± 0.002	<0.1
27	1.19 ± 0.012	0.223 ± 0.006	0.701 ± 0.010	<0.1
28	2.09 ± 0.07	0.360 ± 0.014	1.15 ± 0.042	0.124 ± 0.005
29	0.642 ± 0.023	0.072 ± 0.002	0.320 ± 0.009	<0.1
30	<0.1	<0.1	0.623 ± 0.014	<0.1
31	1.19 ± 0.04	0.132 ± 0.003	<0.2	<0.1
32	1.11 ± 0.04	0.321 ± 0.005	0.707 ± 0.002	0.159 ± 0.007
39	0.939 ± 0.031[c]	0.334 ± 0.005	1.05 ± 0.031[c]	0.180 ± 0.008
40	<0.1	0.091 ± 0.001	<0.1	<0.1
42	1.39 ± 0.04	0.081 ± 0.003	0.699 ± 0.030	<0.1
44	0.901 ± 0.032	0.088 ± 0.001	0.424 ± 0.009	<0.1
47	0.708 ± 0.009	0.074 ± 0.002	0.319 ± 0.002	<0.1
49	1.63 ± 0.04	0.064 ± 0.005	0.764 ± 0.033	<0.1
50	1.22 ± 0.07	0.101 ± 0.001	0.564 ± 0.014	<0.1
54	1.29 ± 0.05[c]	0.461 ± 0.013	1.45 ± 0.05[c]	0.265 ± 0.007
55	1.29 ± 0.05[c]	0.263 ± 0.033	1.39 ± 0.04	0.157 ± 0.009
62	1.10 ± 0.04	0.073 ± 0.003	0.836 ± 0.023	0.036 ± 0.002
64	1.20 ± 0.04	0.114 ± 0.006	0.958 ± 0.021	0.059 ± 0.005
65	1.21 ± 0.05	0.113 ± 0.001	1.06 ± 0.01	0.061 ± 0.004
67	0.915 ± 0.031	0.041 ± 0.001	0.616 ± 0.021	0.023 ± 0.001
69	0.671 ± 0.033	0.015 ± 0.001	0.378 ± 0.006	<0.02
71	0.262 ± 0.012	0.010 ± 0.001	0.109 ± 0.007	<0.02
73	0.602 ± 0.021	0.013 ± 0.001	0.313 ± 0.008	<0.02

TABLE C-5. (Continued)

GC Peak No.[a]	Amount Found,[b] g/100 g, in Given Sample			
	VN-80-40	VN-80-41	VN-80-48	VN-80-50
77	0.393 ± 0.020	<0.01	0.188 ± 0.010	<0.01
78	0.508 ± 0.022	<0.01	0.269 ± 0.004	<0.01
79	(d)	<0.01	0.148 ± 0.013	<0.01
80	0.514 ± 0.022	<0.01	0.258 ± 0.012	<0.01
81	0.422 ± 0.024	<0.01	0.200 ± 0.011	<0.01
82	0.247 ± 0.007	<0.01	0.075 ± 0.006	<0.01
84	0.257 ± 0.021	<0.01	0.095 ± 0.007	<0.01
90	0.113 ± 0.004	<0.005	0.046 ± 0.001	<0.005
91	0.083 ± 0.004	<0.005	0.035 ± 0.008	<0.005
92	0.109 ± 0.003	<0.005	0.041 ± 0.005	<0.005

(a) The tentative identifications of the GC peaks are given in Table 2.
(b) Average of three runs.
(c) The detector was saturated; the correct value is therefore considerably higher.
(d) This peak was not quantified because the data system did not resolve it from Peak No. 80.

TABLE C-6. AROMATIC HYDROCARBON COMPOSITION OF FUEL SAMPLES DETERMINED BY GC-UVD ANALYSIS OF NEAT SAMPLES, SET F

GC Peak No.[a]	Amount Found,[b] g/100 g, in Given Sample			
	VN-80-56	VN-80-61	VN-80-62	VN-80-73
0	<0.01	0.103 ± 0.005	<0.01	<0.1
1	0.033 ± 0.001	1.30 ± 0.01	<0.01	1.53 ± 0.002
2	0.036 ± 0.003	0.219 ± 0.002	<0.01	1.75 ± 0.01
3	0.108 ± 0.005	1.15 ± 0.04	<0.1	4.82 ± 0.04
4	0.069 ± 0.003	0.502 ± 0.014	<0.1	2.33 ± 0.01
5	0.019 ± 0.001	0.027 ± 0.003	<0.01	0.075 ± 0.001
6	0.033 ± 0.001	0.111 ± 0.003	0.087 ± 0.002	0.292 ± 0.005
7	0.102 ± 0.003	0.347 ± 0.023	0.326 ± 0.006	1.30 ± 0.01
8	0.075 ± 0.002	0.210 ± 0.009	0.249 ± 0.001	1.04 ± 0.01
9	0.067 ± 0.001	0.132 ± 0.001	0.293 ± 0.002	0.575 ± 0.005
10	0.316 ± 0.005	0.653 ± 0.013	1.042 ± 0.008	2.89 ± 0.04
13	0.171 ± 0.005	0.265 ± 0.014	0.874 ± 0.021	0.961 ± 0.028
16	<0.1	1.109 ± 0.001	0.359 ± 0.005	0.124 ± 0.003
17	0.105 ± 0.001	0.171 ± 0.001	0.428 ± 0.004	0.195 ± 0.005
18	0.084 ± 0.001	0.155 ± 0.001	0.383 ± 0.008	0.130 ± 0.003
19	0.113 ± 0.003	0.145 ± 0.002	0.387 ± 0.008	0.260 ± 0.003
20	0.084 ± 0.001	0.075 ± 0.004	0.295 ± 0.006	<0.1
21	0.151 ± 0.006	0.145 ± 0.001	0.479 ± 0.014	0.275 ± 0.005
22	0.123 ± 0.004	0.141 ± 0.007	0.363 ± 0.002	0.306 ± 0.005
23	<0.1	<0.1	0.176 ± 0.001	<0.1
24	<0.1	<0.1	0.361 ± 0.02	<0.1
25	0.114 ± 0.004	0.164 ± 0.001	<0.1	0.134 ± 0.007
27	<0.1	0.109 ± 0.006	0.291 ± 0.003	0.305 ± 0.016
28	0.411 ± 0.017	0.164 ± 0.011	0.430 ± 0.006	0.437 ± 0.009
29	<0.1	0.139 ± 0.008	0.359 ± 0.004	0.110 ± 0.004
31	<0.1	0.282 ± 0.001	<0.1	0.219 ± 0.009
32	0.902 ± 0.033	0.255 ± 0.011	<0.1	0.299 ± 0.014
33	<0.1	0.609 ± 0.009	0.609 ± 0.009	0.198 ± 0.013
34	<0.1	<0.1	0.661 ± 0.008	<0.1
39	0.315 ± 0.007	0.078 ± 0.001	0.271 ± 0.008	0.291 ± 0.001
40	0.176 ± 0.005	0.597 ± 0.022	0.597 ± 0.022	<0.1
42	0.168 ± 0.003	0.283 ± 0.011	0.509 ± 0.009	0.179 ± 0.003
44	0.217 ± 0.006	0.241 ± 0.023	0.375 ± 0.004	0.202 ± 0.009
47	0.360 ± 0.009	0.172 ± 0.019	0.235 ± 0.002	0.297 ± 0.005
49	0.157 ± 0.018	0.135 ± 0.003	0.259 ± 0.003	0.210 ± 0.006
50	0.227 ± 0.024	0.350 ± 0.011	0.604 ± 0.006	0.586 ± 0.026
54	0.576 ± 0.001	0.123 ± 0.007	0.327 ± 0.008	1.10 ± 0.01
55	0.425 ± 0.007	0.065 ± 0.001	0.177 ± 0.005	0.713 ± 0.006
62	0.128 ± 0.008	<0.02	0.04 ± 0.001	0.509 ± 0.009
64	0.169 ± 0.003	0.031 ± 0.003	0.064 ± 0.001	0.825 ± 0.006
65	0.242 ± 0.007	0.032 ± 0.002	0.095 ± 0.001	0.854 ± 0.021
67	0.086 ± 0.003	<0.02	<0.02	0.387 ± 0.007
69	0.038 ± 0.003	<0.02	<0.02	0.211 ± 0.003
71	0.022 ± 0.005	<0.01	<0.02	0.127 ± 0.003
73	0.033 ± 0.003	<0.01	<0.02	0.389 ± 0.003

TABLE C-6. (Continued)

GC Peak No.[a]	Amount Found,[b] g/100 g, in Given Sample			
	VN-80-56	VN-80-61	VN-80-62	VN-80-73
77	0.028 ± 0.003	<0.01	<0.01	0.238 ± 0.007
78	<0.02	<0.01	<0.01	0.330 ± 0.001
79	0.023 ± 0.002	<0.01	<0.01	0.190 ± 0.002
80	<0.02	<0.01	<0.01	0.303 ± 0.007
81	0.019 ± 0.001	<0.01	<0.01	0.271 ± 0.017
82	<0.01	<0.01	<0.01	0.134 ± 0.002
84	<0.01	<0.01	<0.01	0.162 ± 0.004
90	<0.005	<0.005	<0.005	0.098 ± 0.001
91	<0.005	<0.005	<0.005	0.069 ± 0.007
92	<0.005	<0.005	<0.005	0.104 ± 0.018

(a) The tentative identifications of the GC peaks are given in Table 2.
(b) Average of three runs.

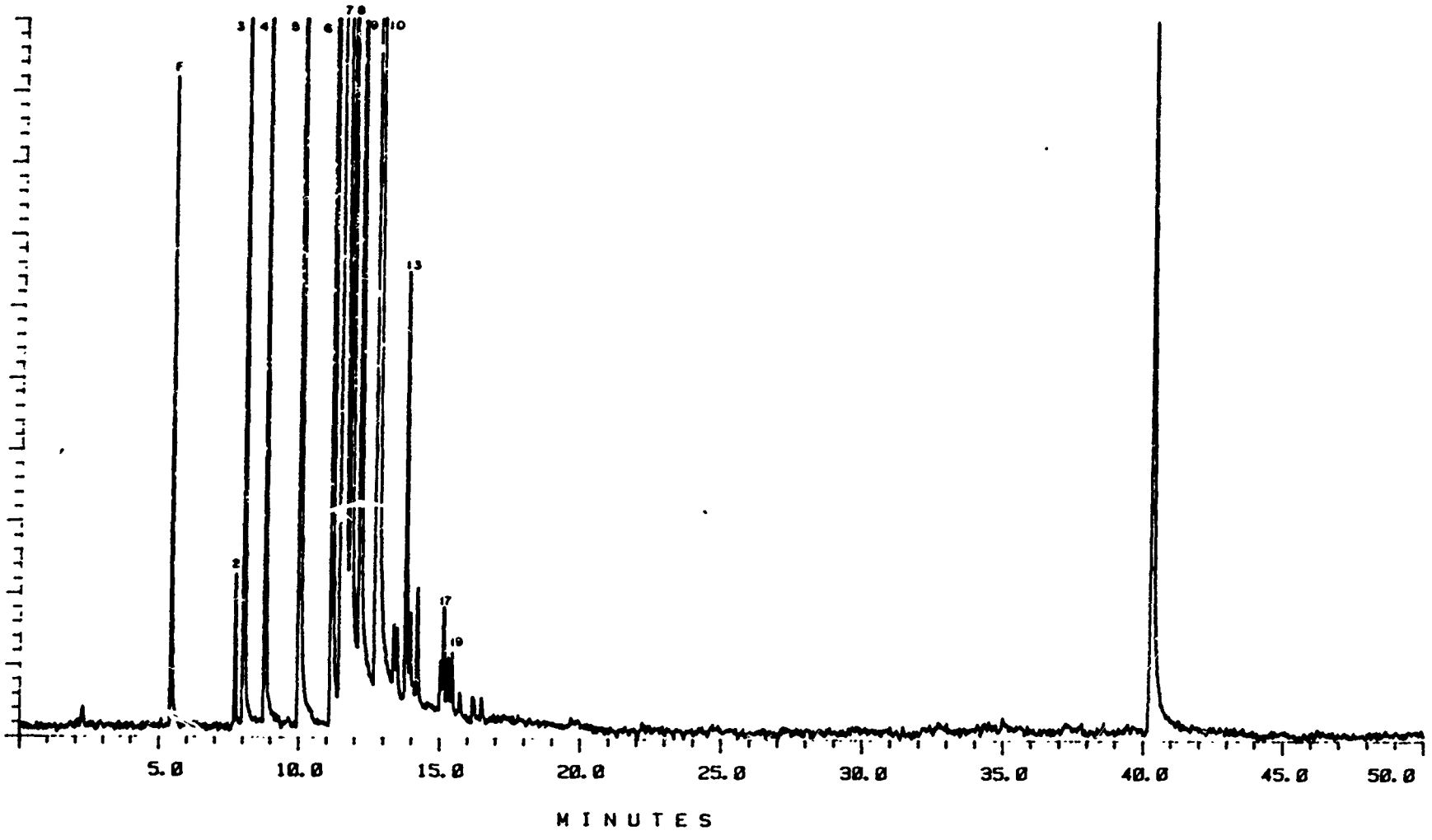


Figure C-1. GC-UVD Chromatogram of Fuel Sample VN-80-39 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

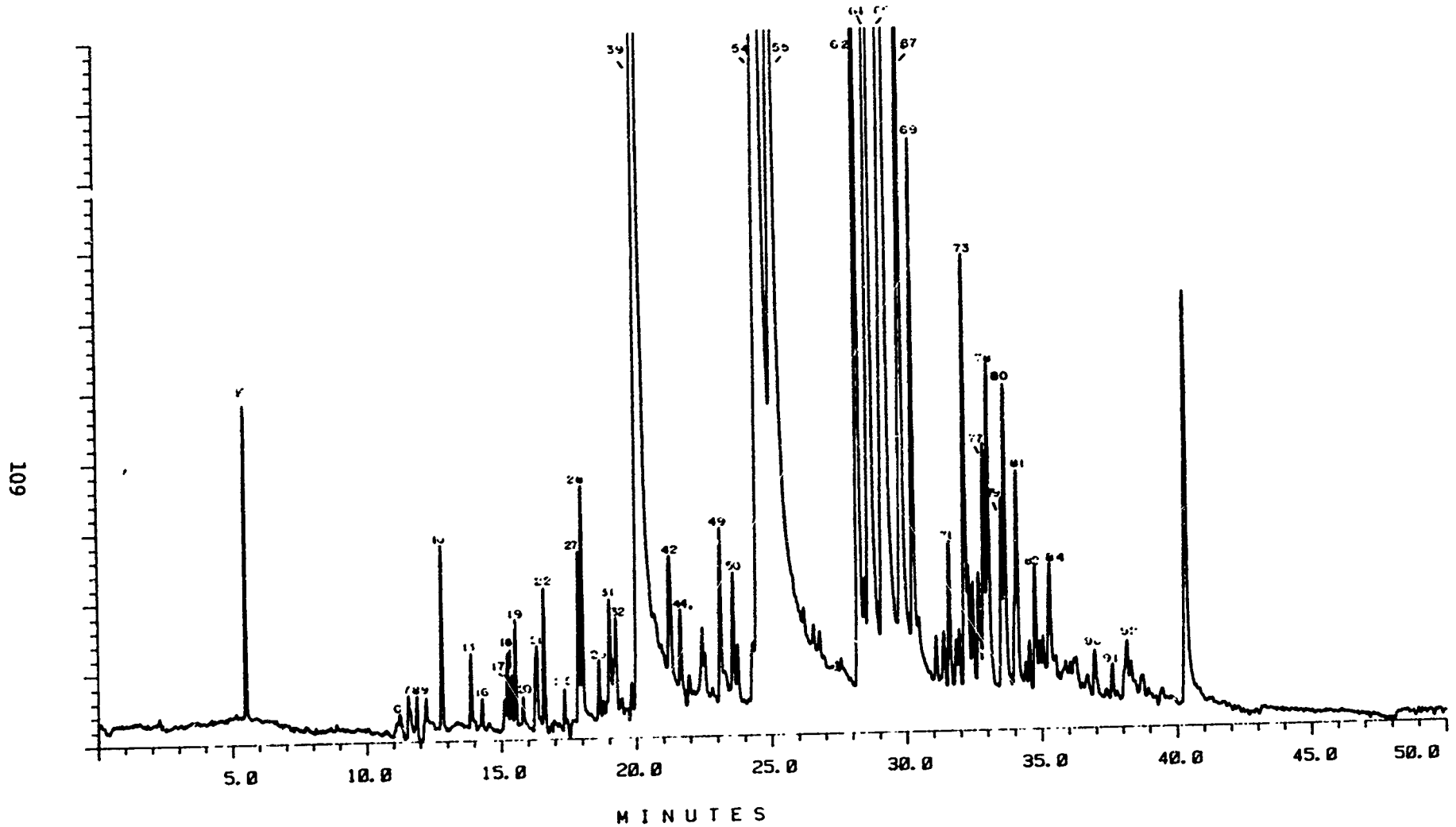


Figure C-2. GC-UVD Chromatogram of Fuel Sample VN-80-40 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

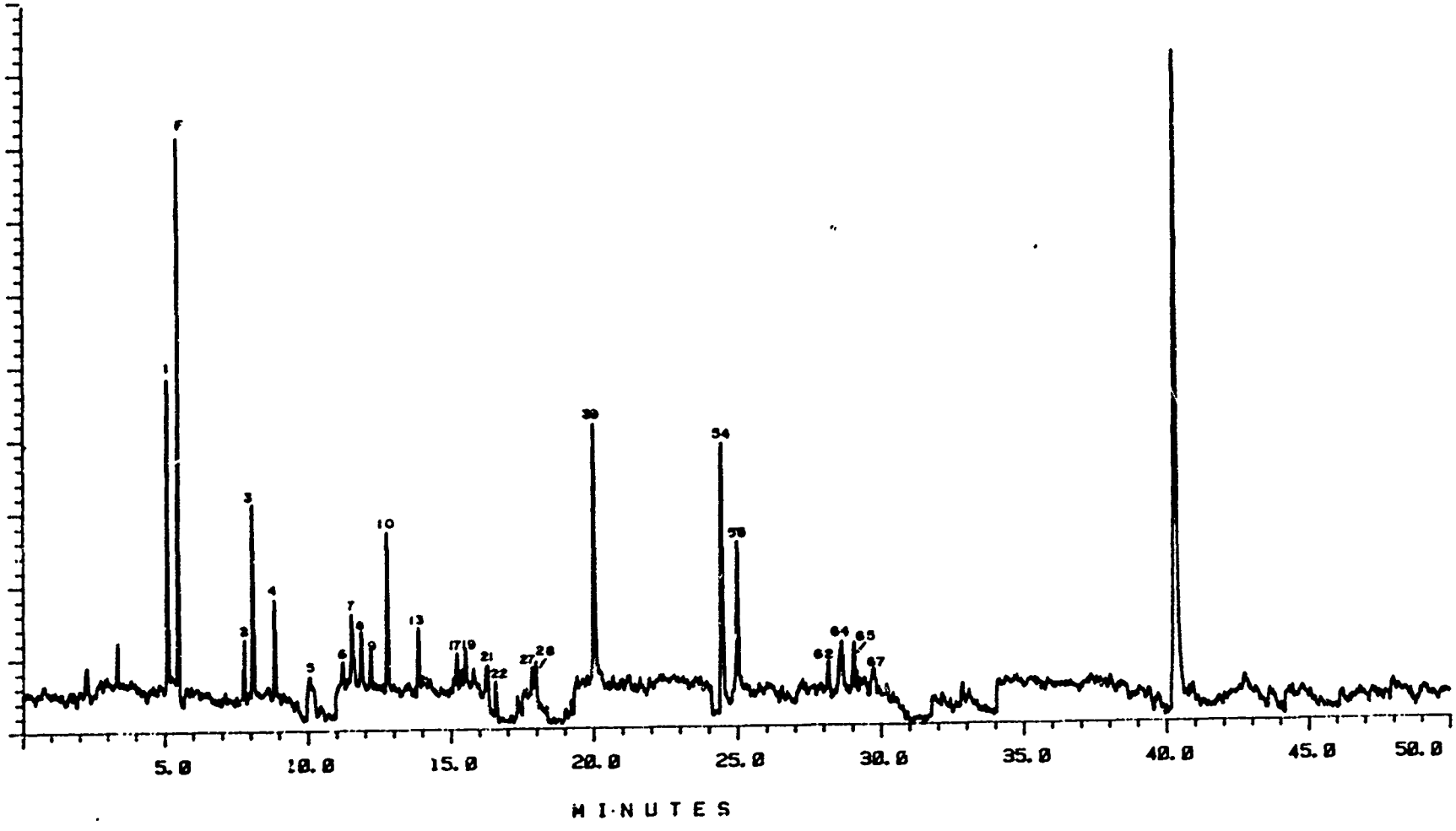


Figure C-3. GC-UVD Chromatogram of Fuel Sample VN-80-41 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

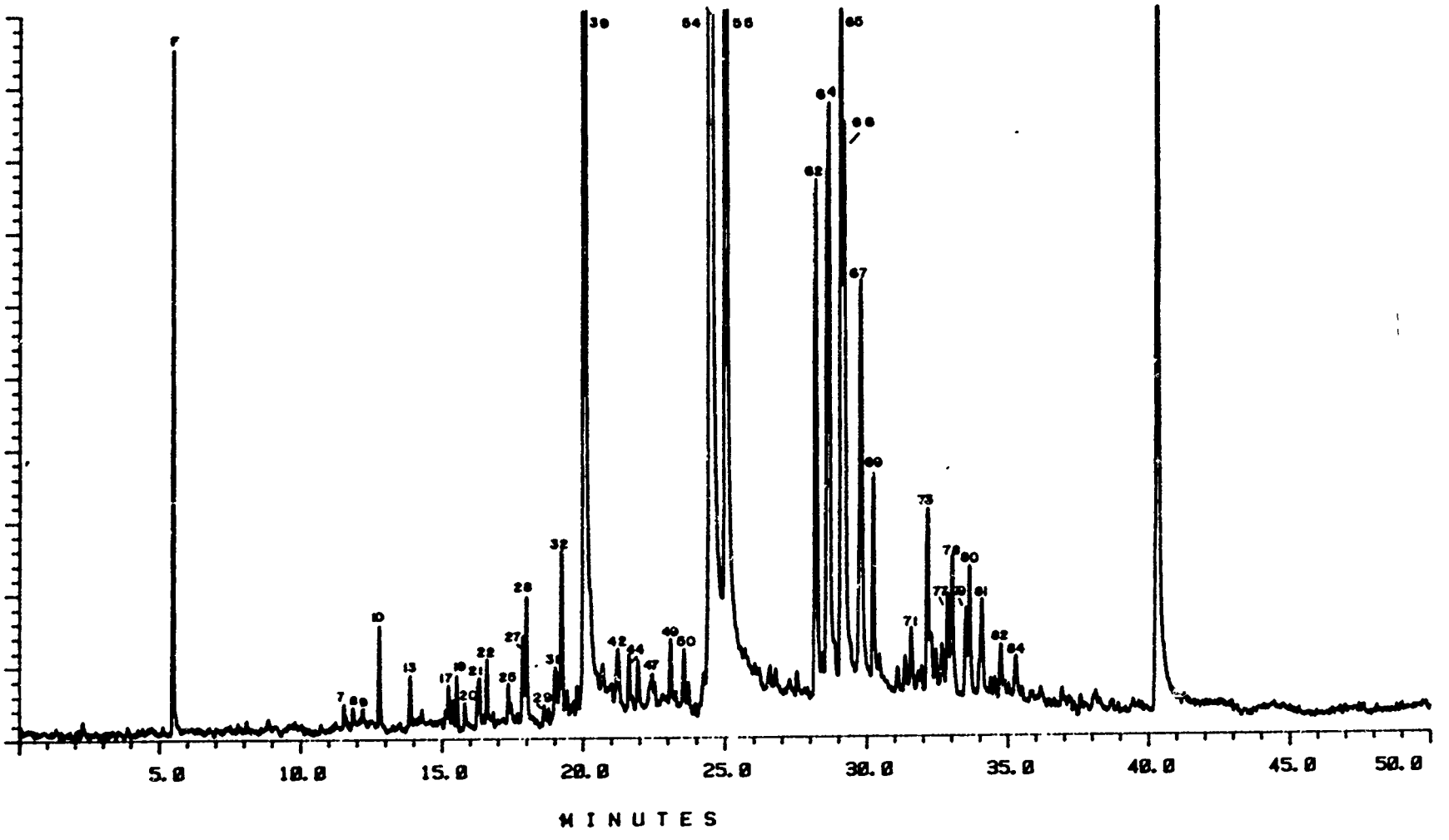


Figure C-4. GC-UVD Chromatogram of Fuel Sample VN-80-47 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

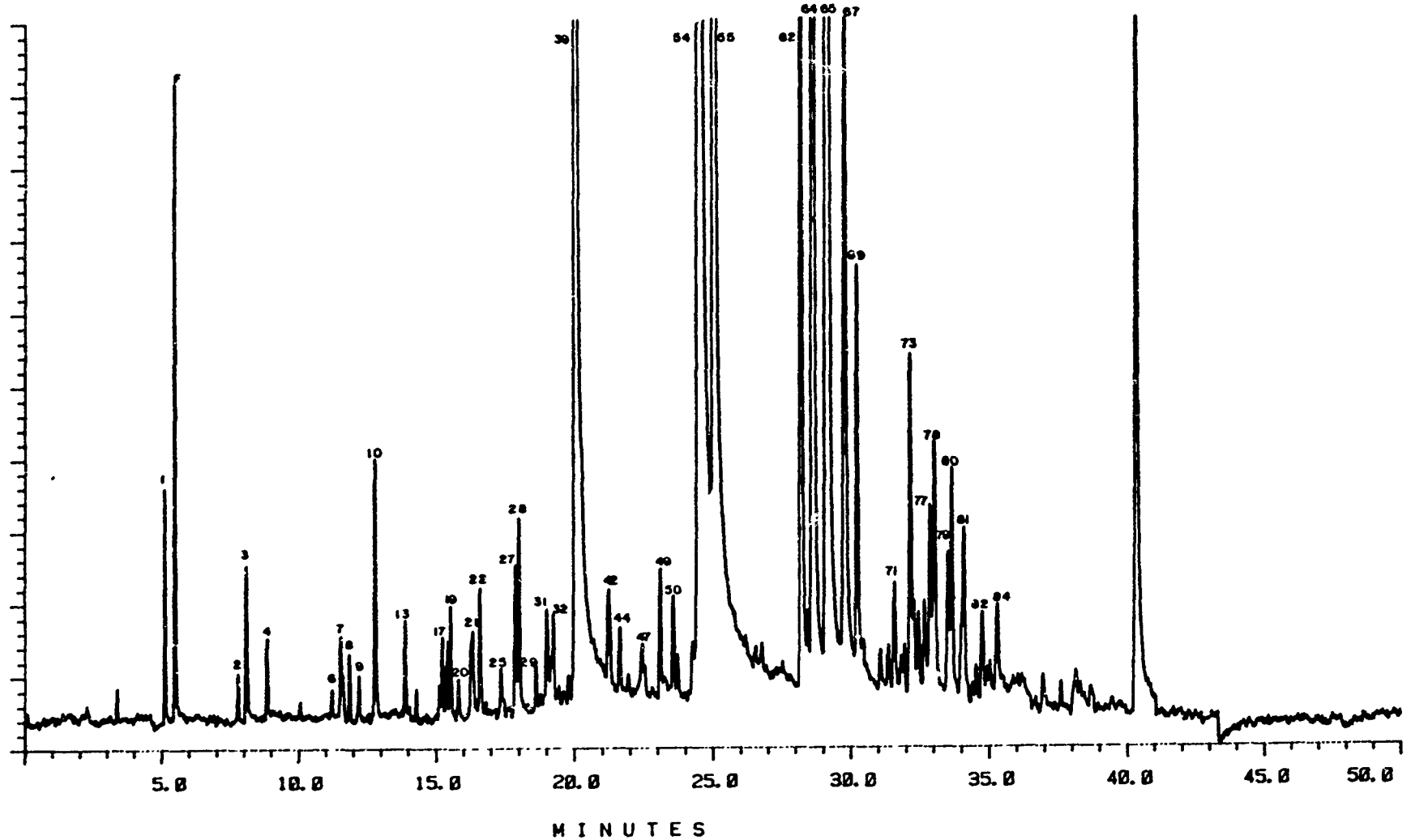


Figure C-5. GC-UVD Chromatogram of Fuel Sample VN-80-48 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

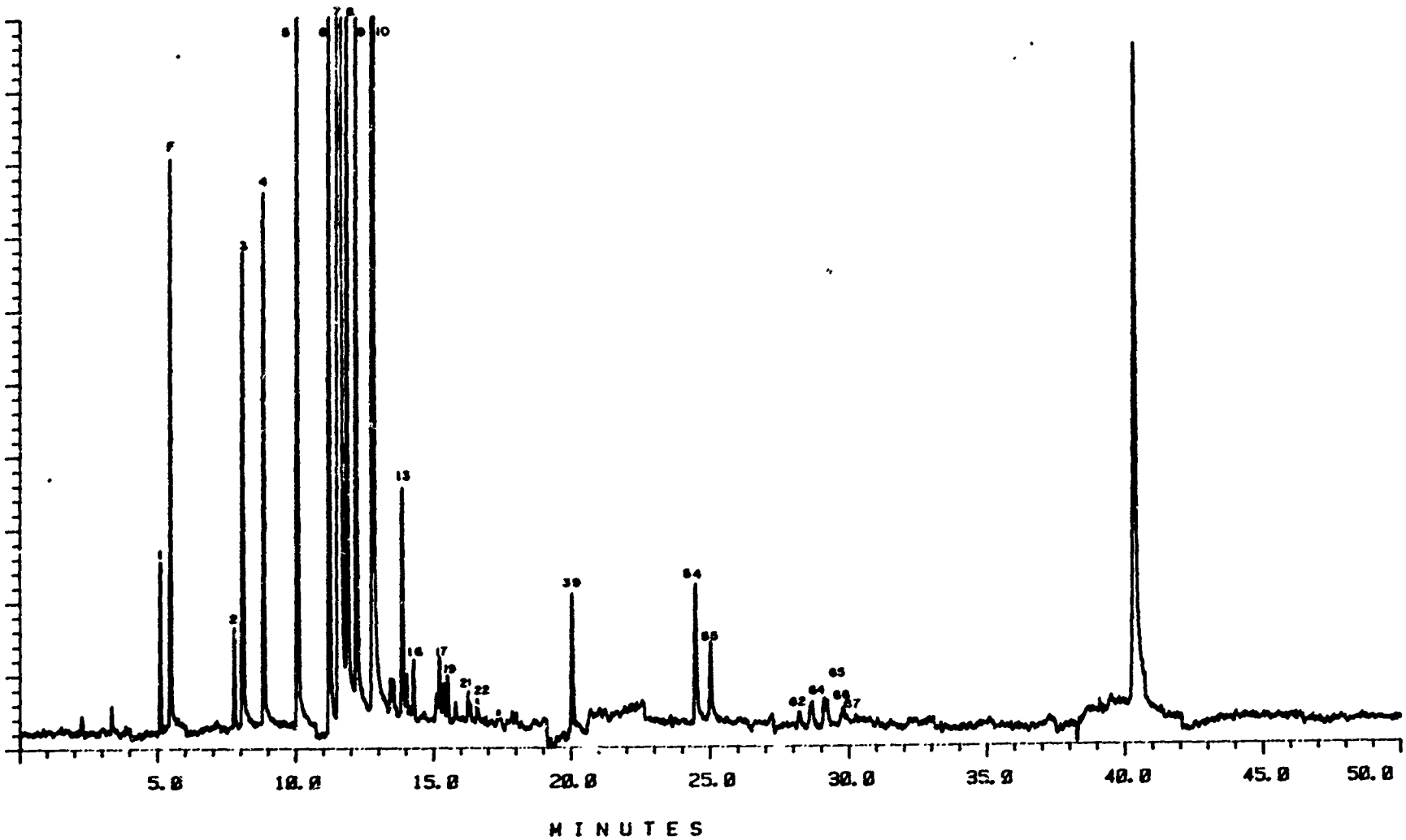


Figure C-6. GC-UVD Chromatogram of Fuel Sample VN-80-50 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

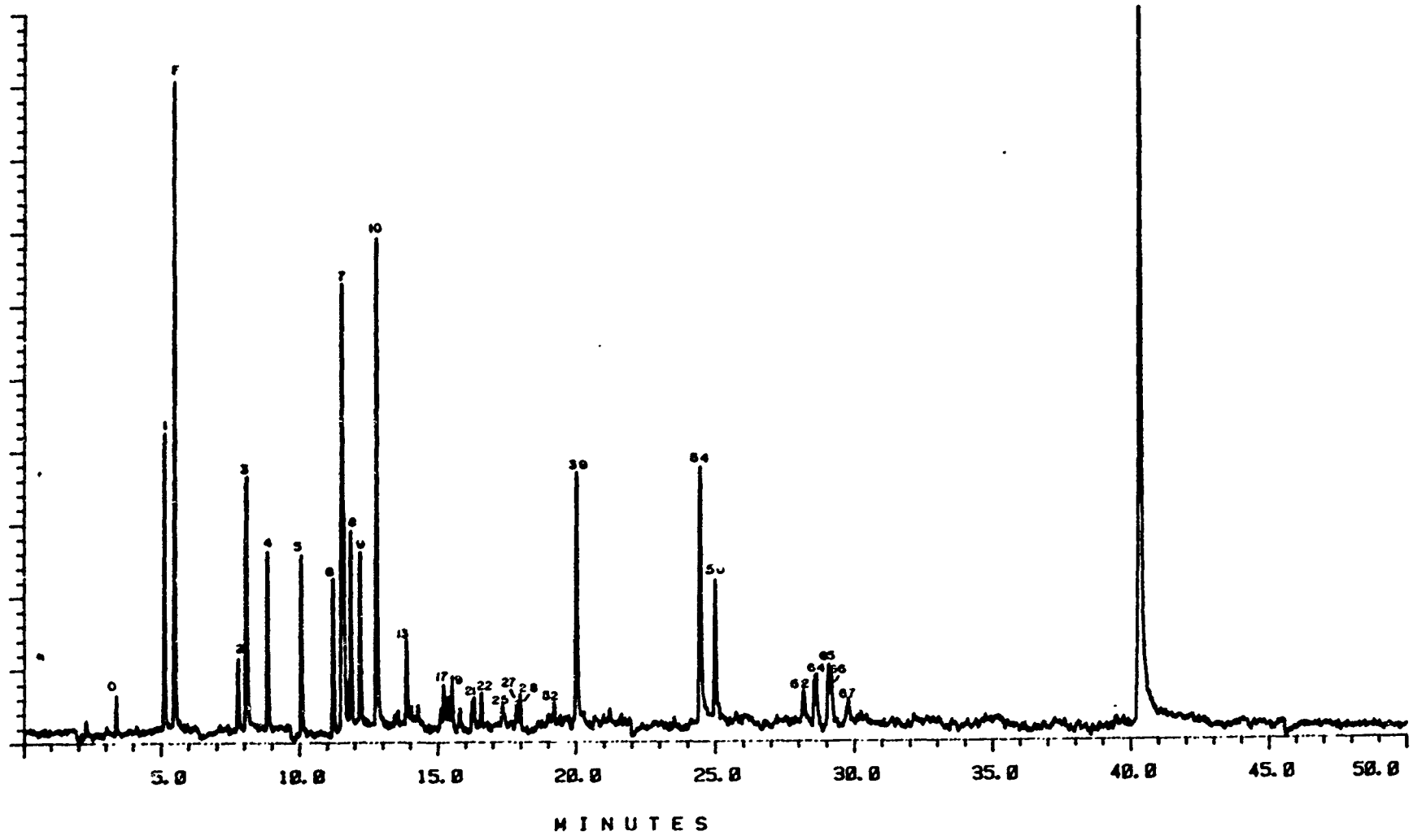


Figure C-7. GC-UVD Chromatogram of Fuel Sample VN-80-52 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

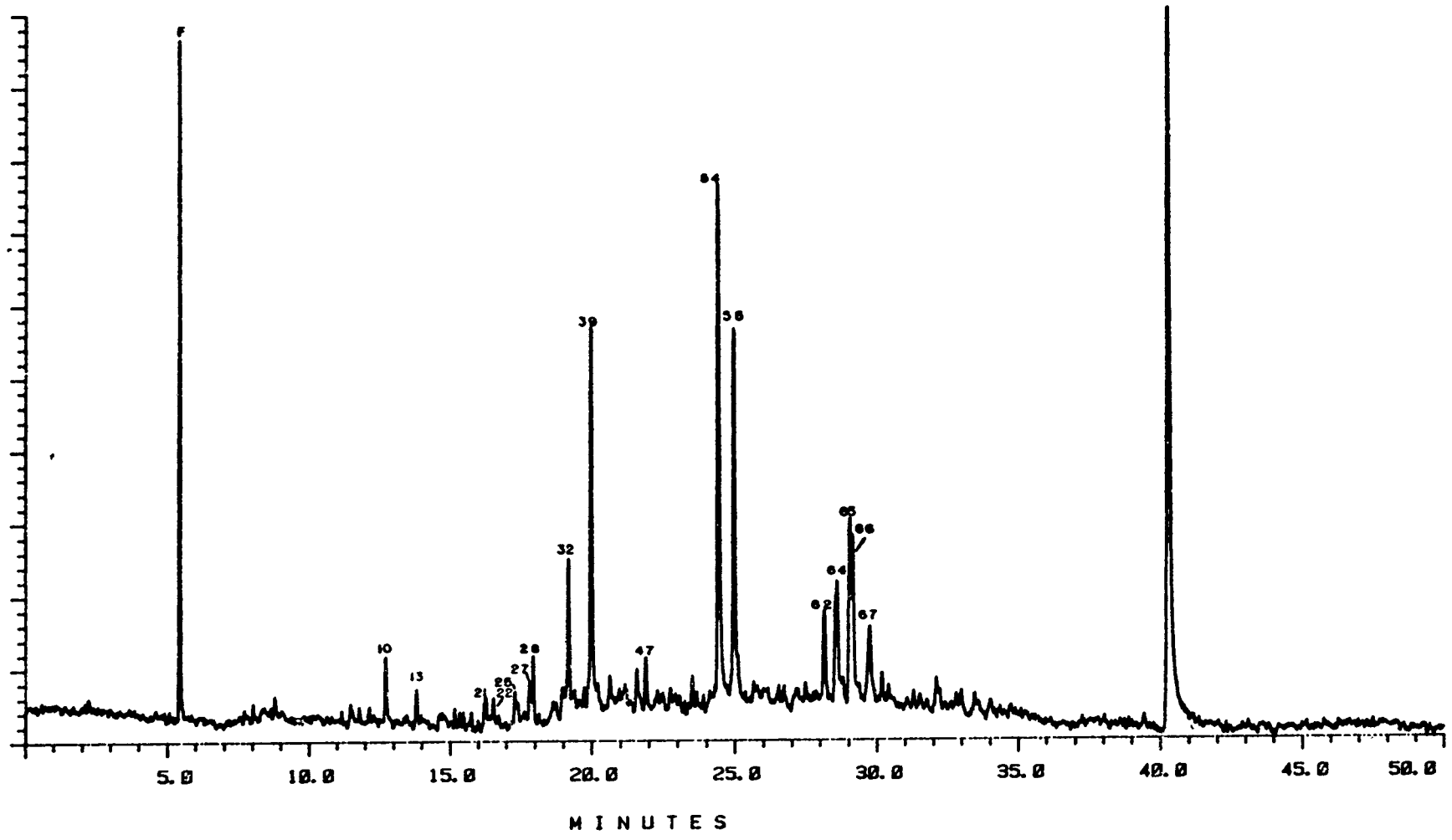


Figure C-8. GC-UVD Chromatogram of Fuel Sample VN-80-56 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

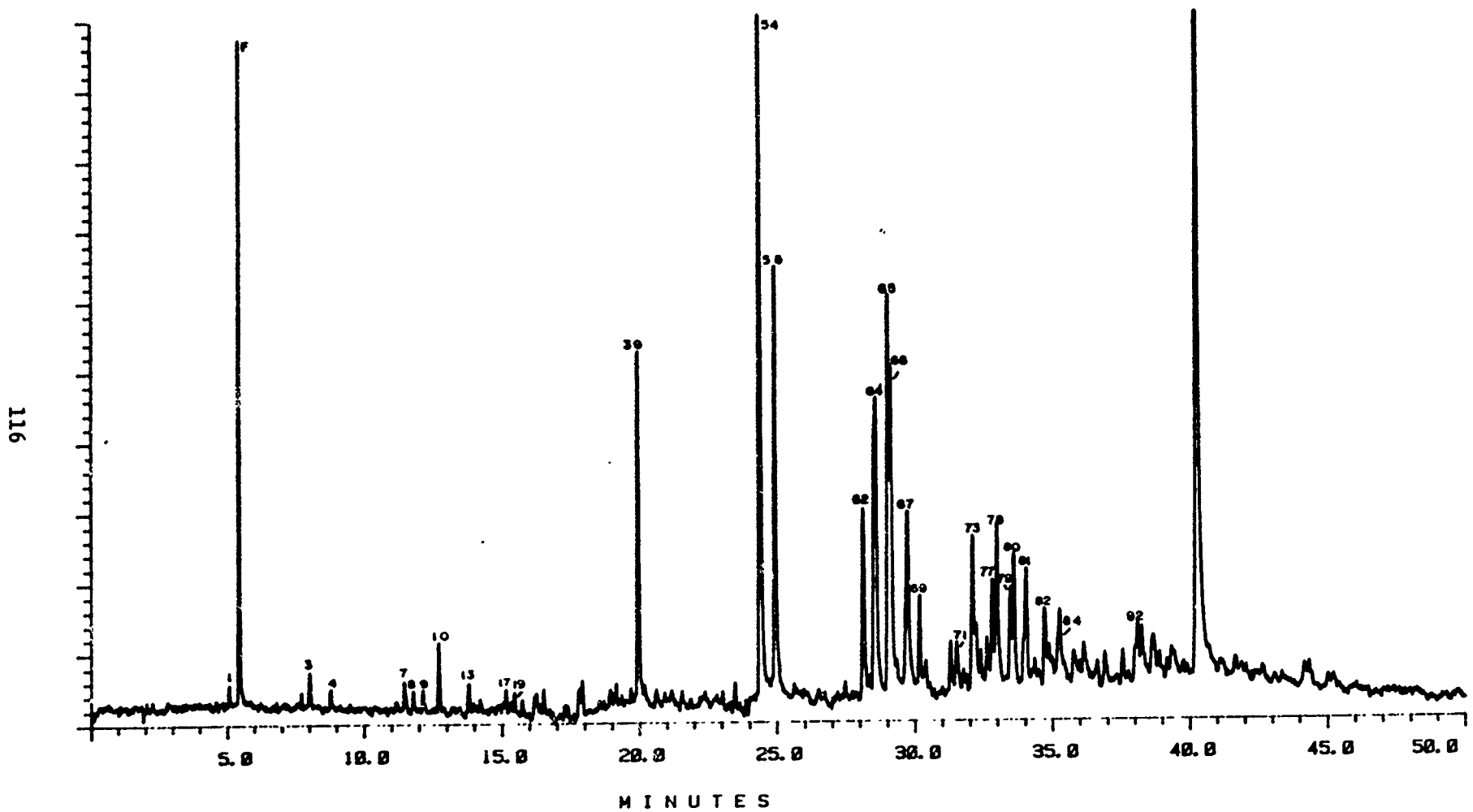


Figure C-9. GC-UVD Chromatogram of Fuel Sample VN-80-59 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

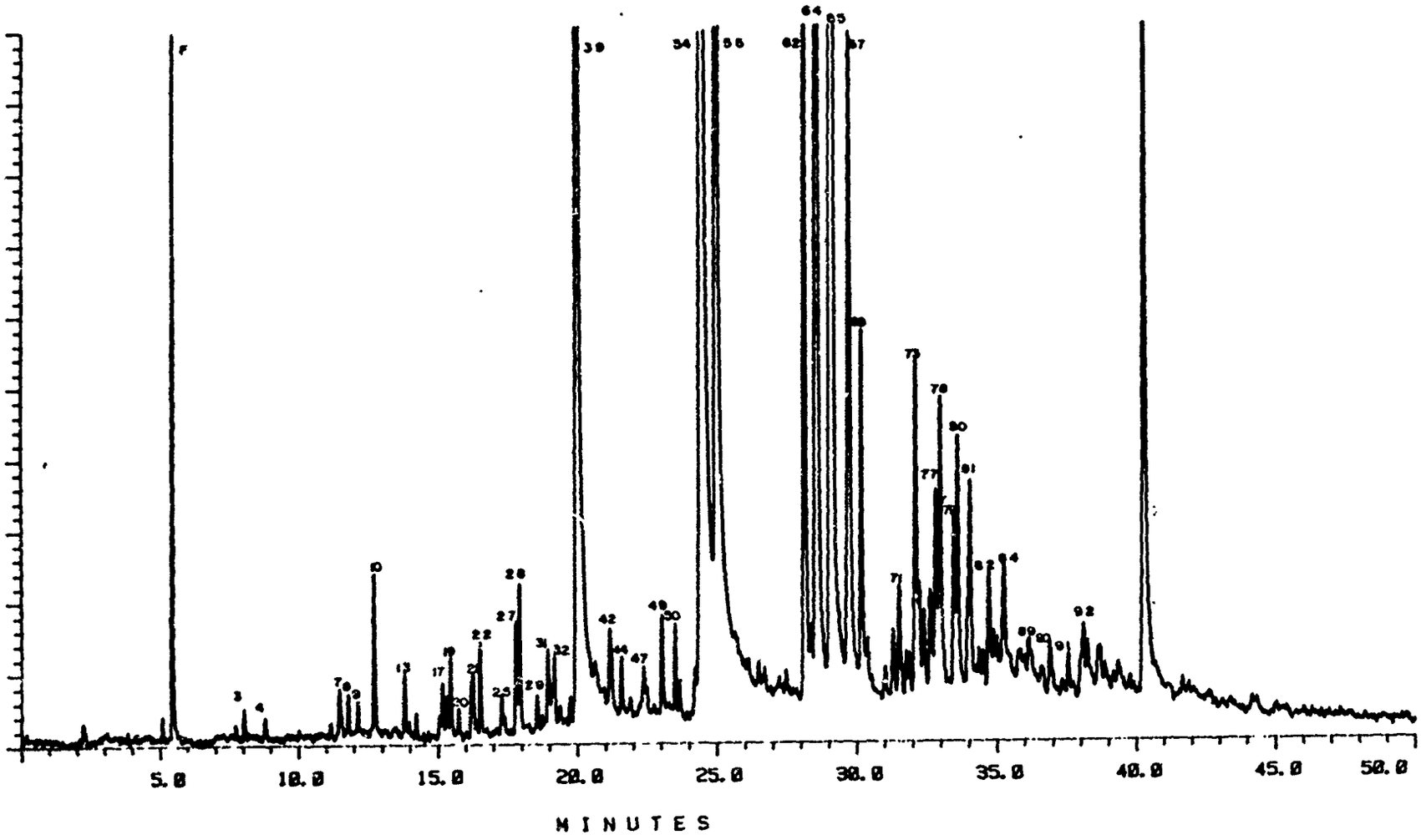


Figure C-10. GC-UVD Chromatogram of Fuel Sample VN-80-60 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

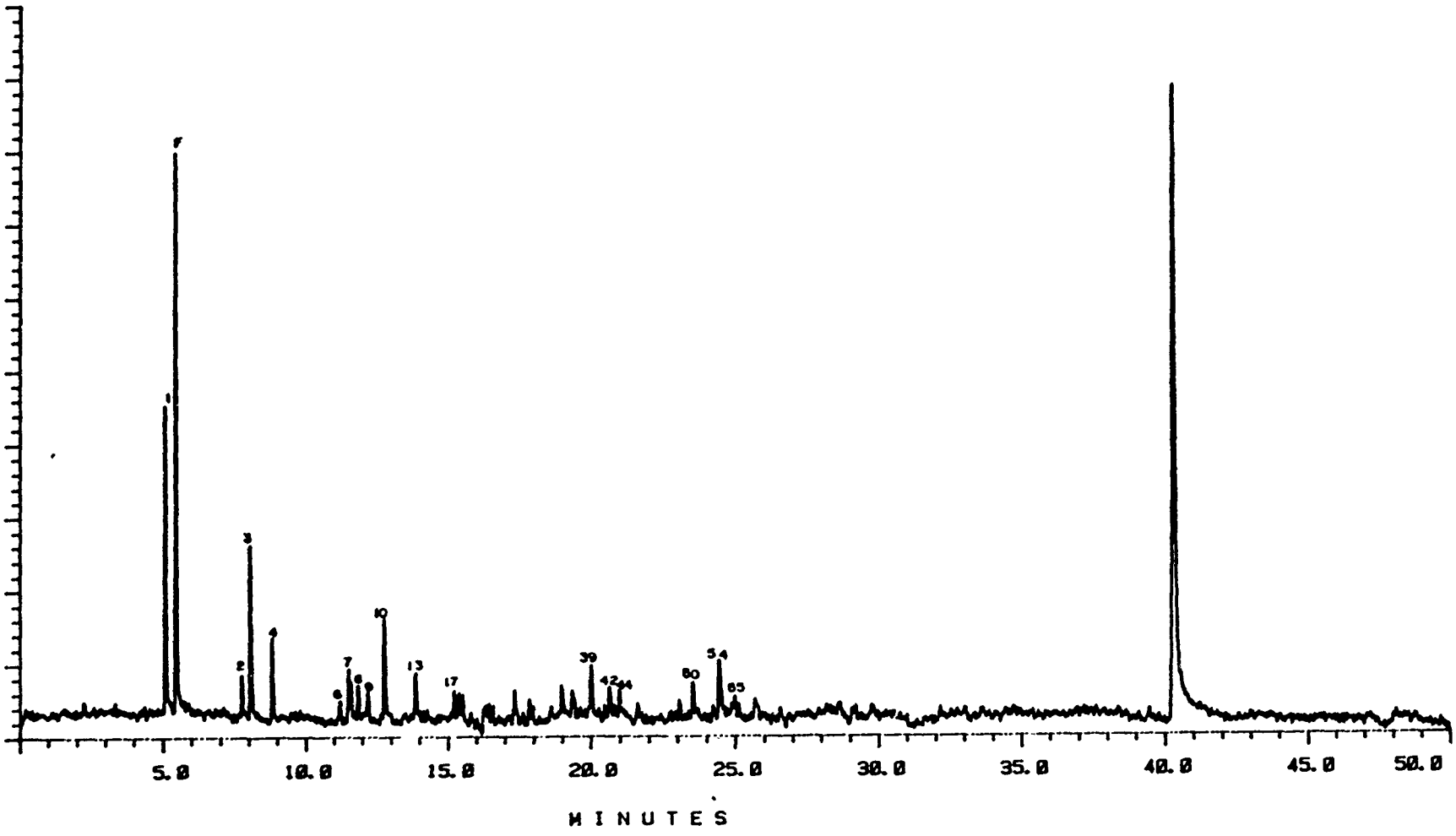


Figure C-11. GC-UVD Chromatogram of Fuel Sample VN-80-61 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

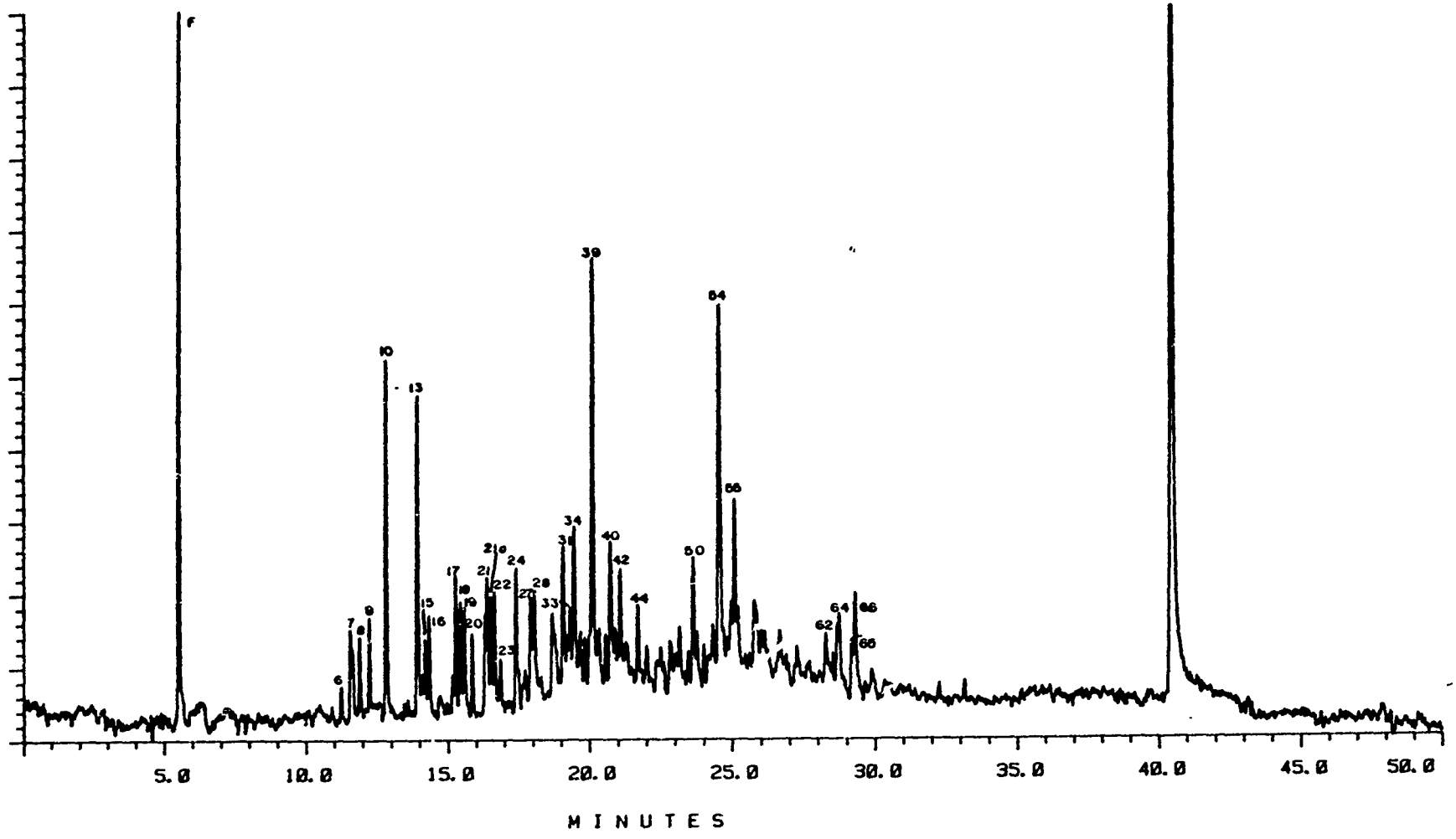


Figure C-12. GC-UVD Chromatogram of Fuel Sample VN-80-62 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

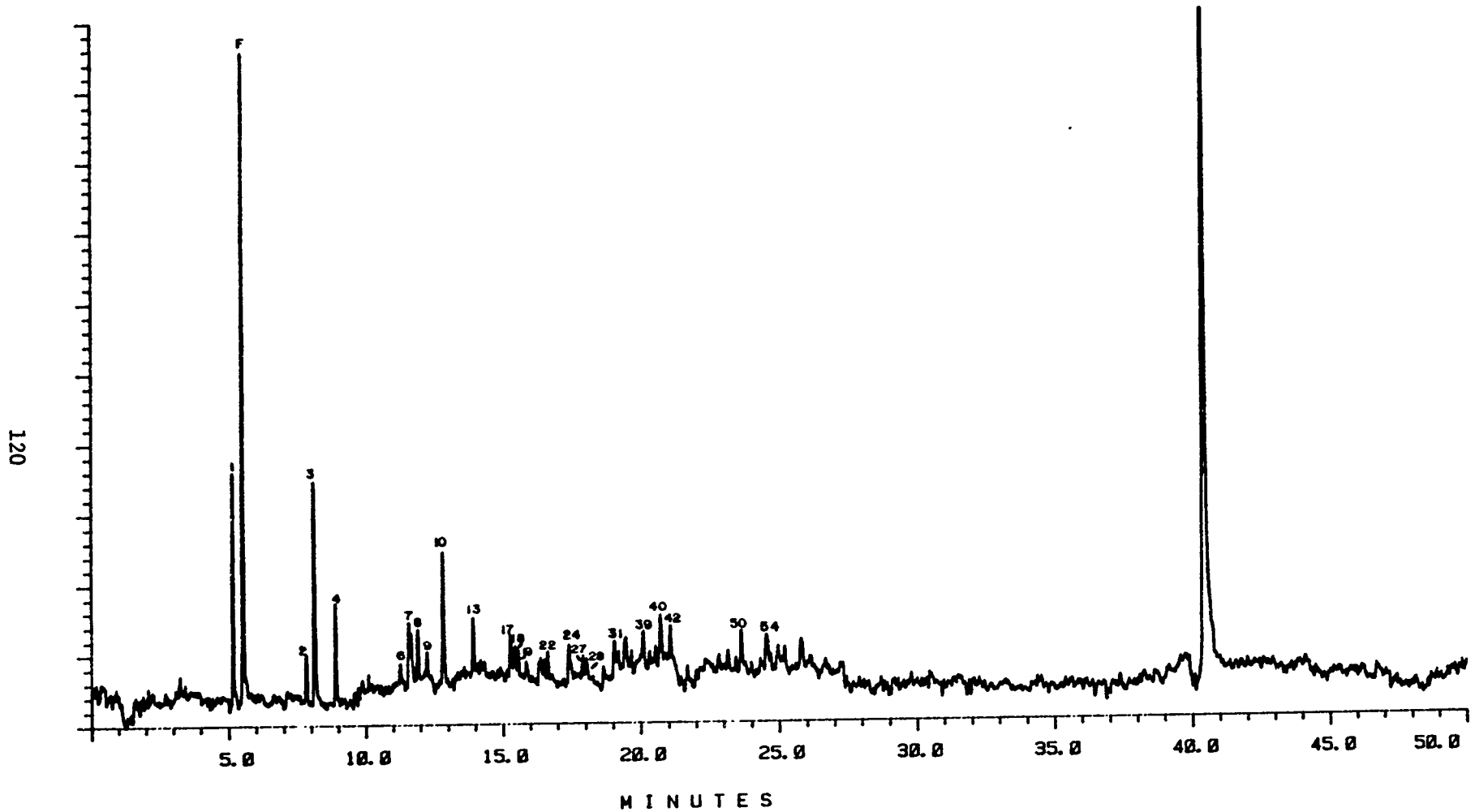


Figure C-13. GC-UVD Chromatogram of Fuel Sample VN-80-67 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

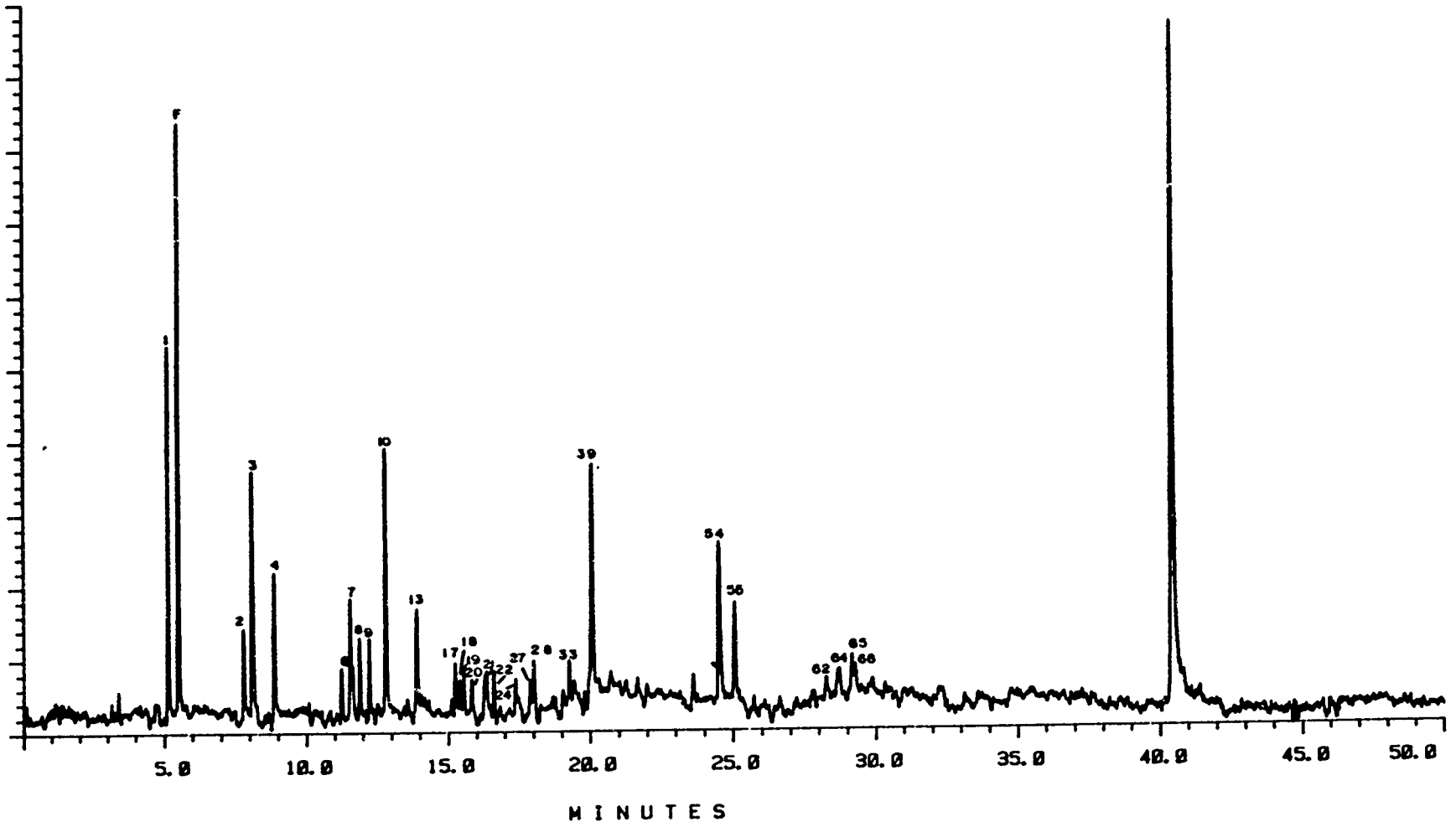


Figure C-14. GC-UVD Chromatogram of Fuel Sample VN-80-68 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

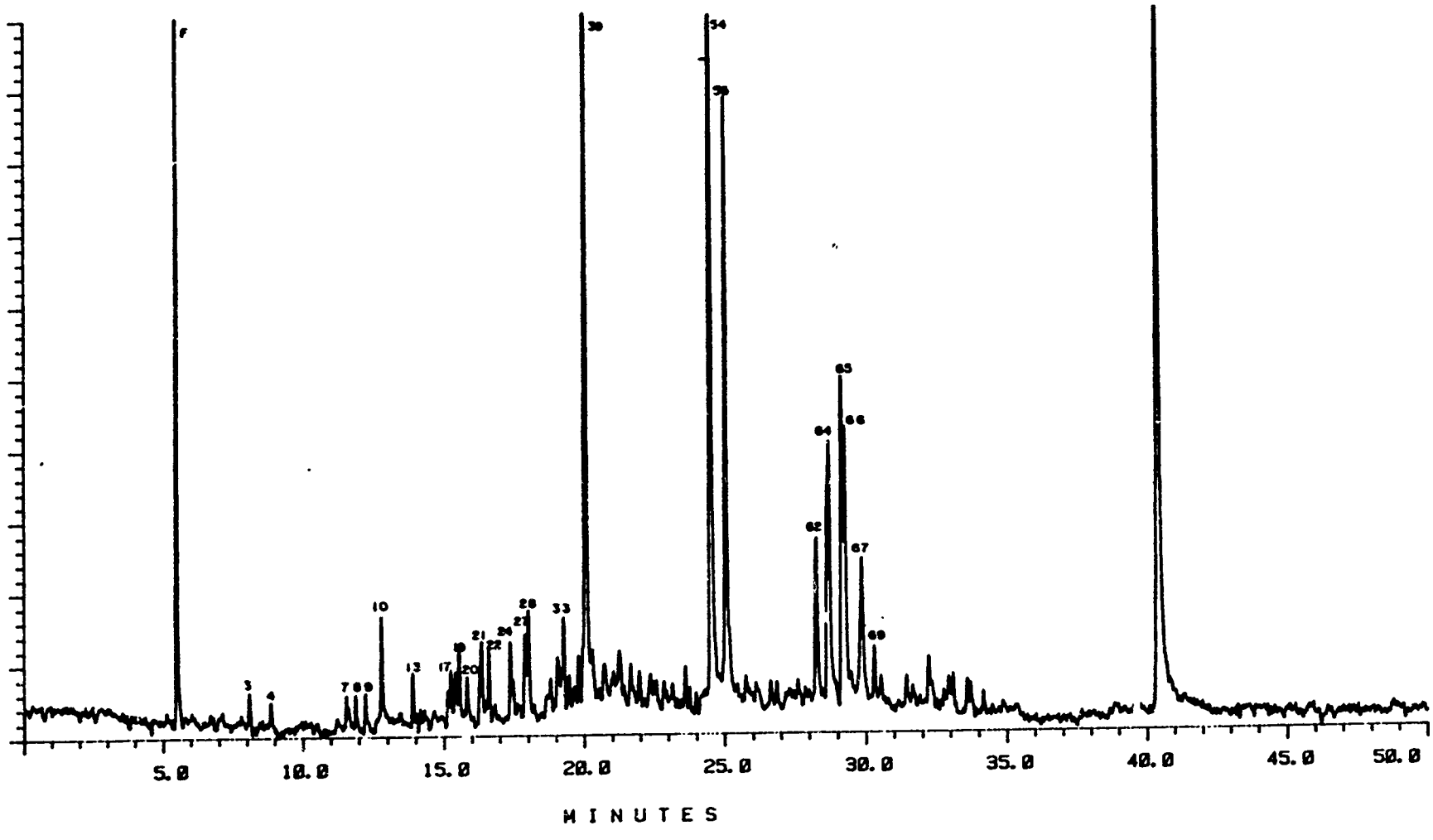


Figure C-15. GC-UVD Chromatogram of Fuel Sample VN-80-69 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

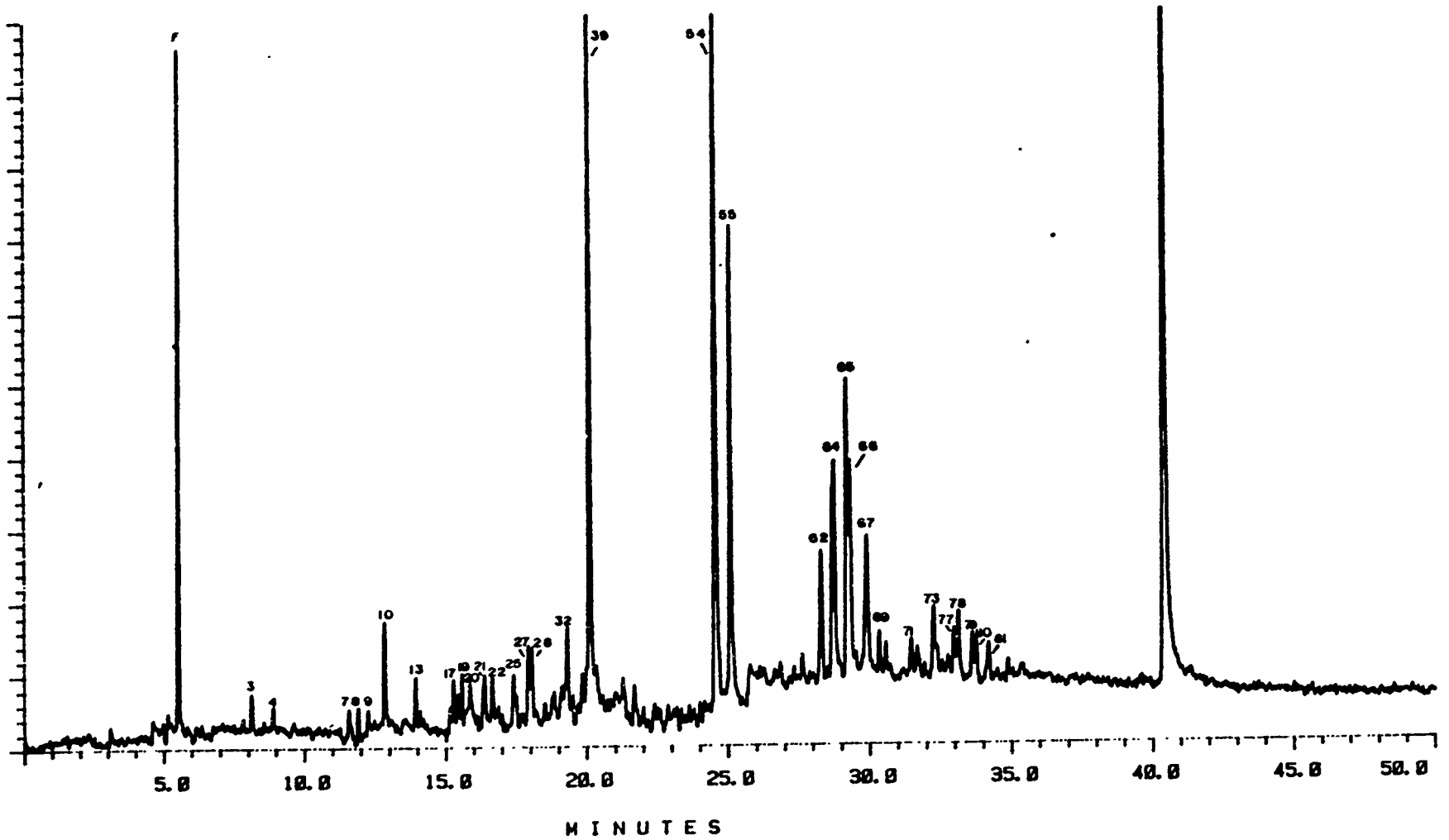


Figure C-16. GC-UVD Chromatogram of Fuel Sample VN-80-70 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification numbered components).

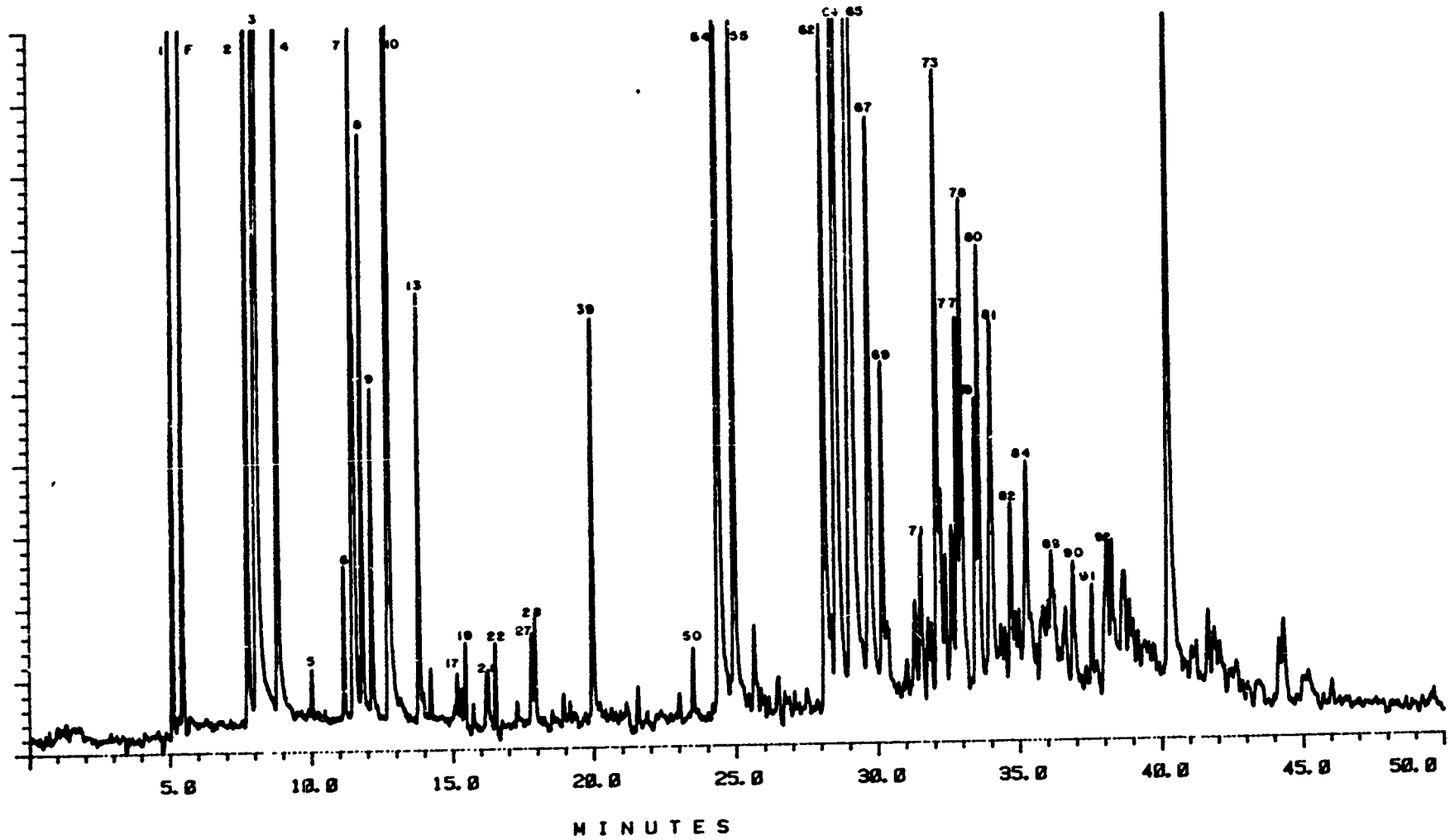


Figure C-17. GC-UVD Chromatogram of Fuel Sample VN-80-71 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identificatcn of numbered components).

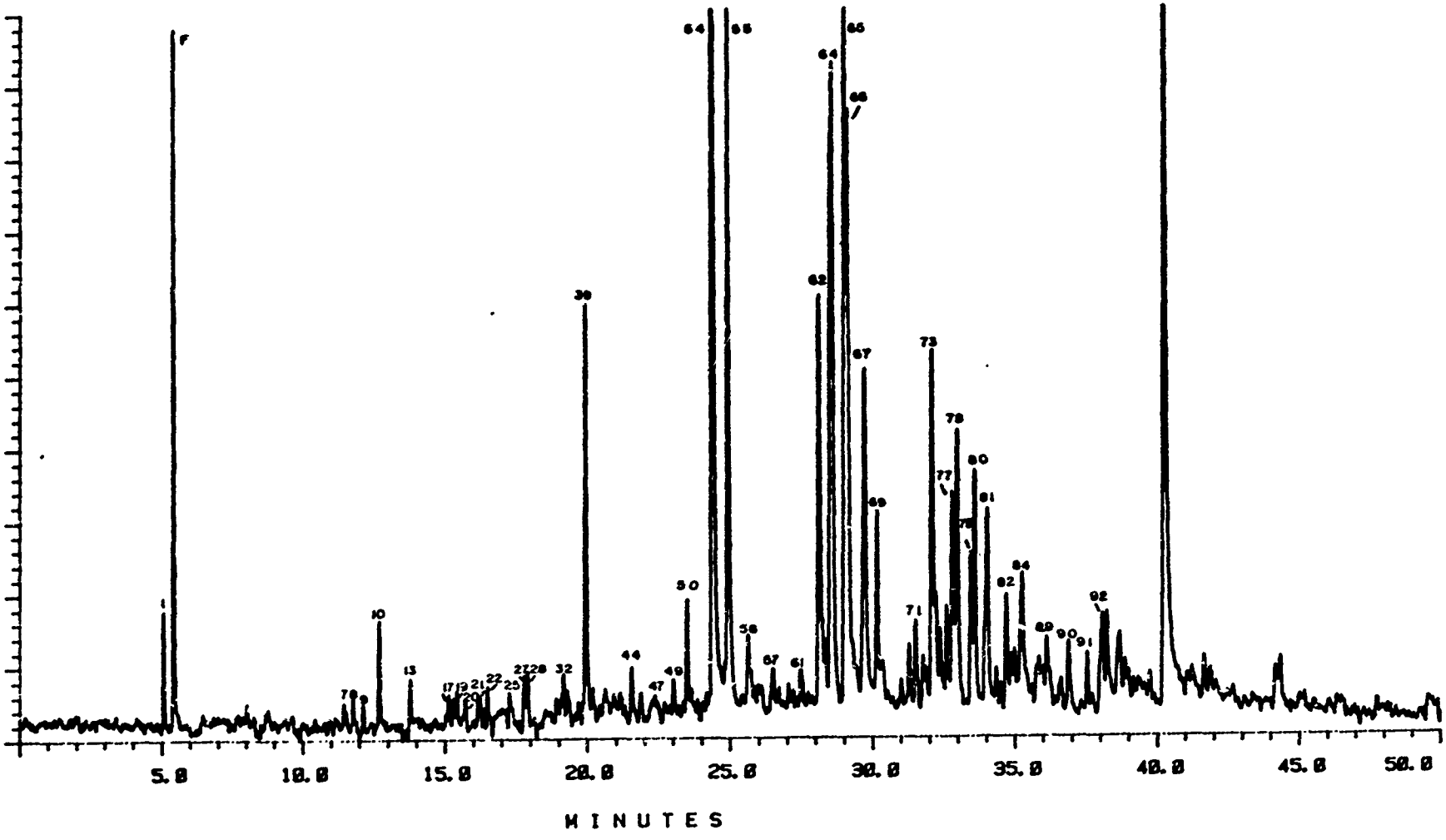


Figure C-18. GC-UVD Chromatogram of Fuel Sample VN-80-72 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification numbered components).

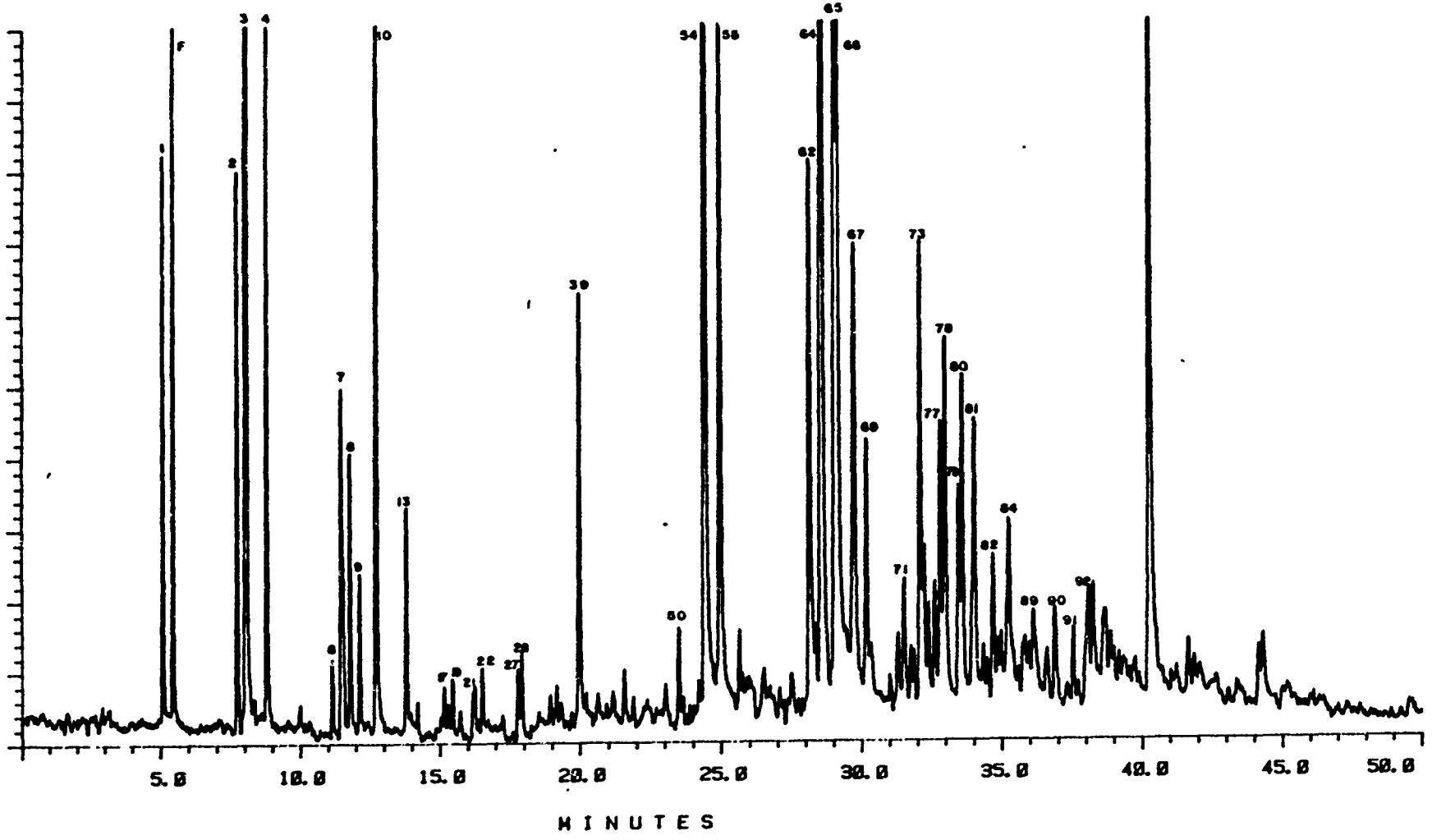


Figure C-19. GC-UVD Chromatogram of Fuel Sample VN-80-73 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification of numbered components).

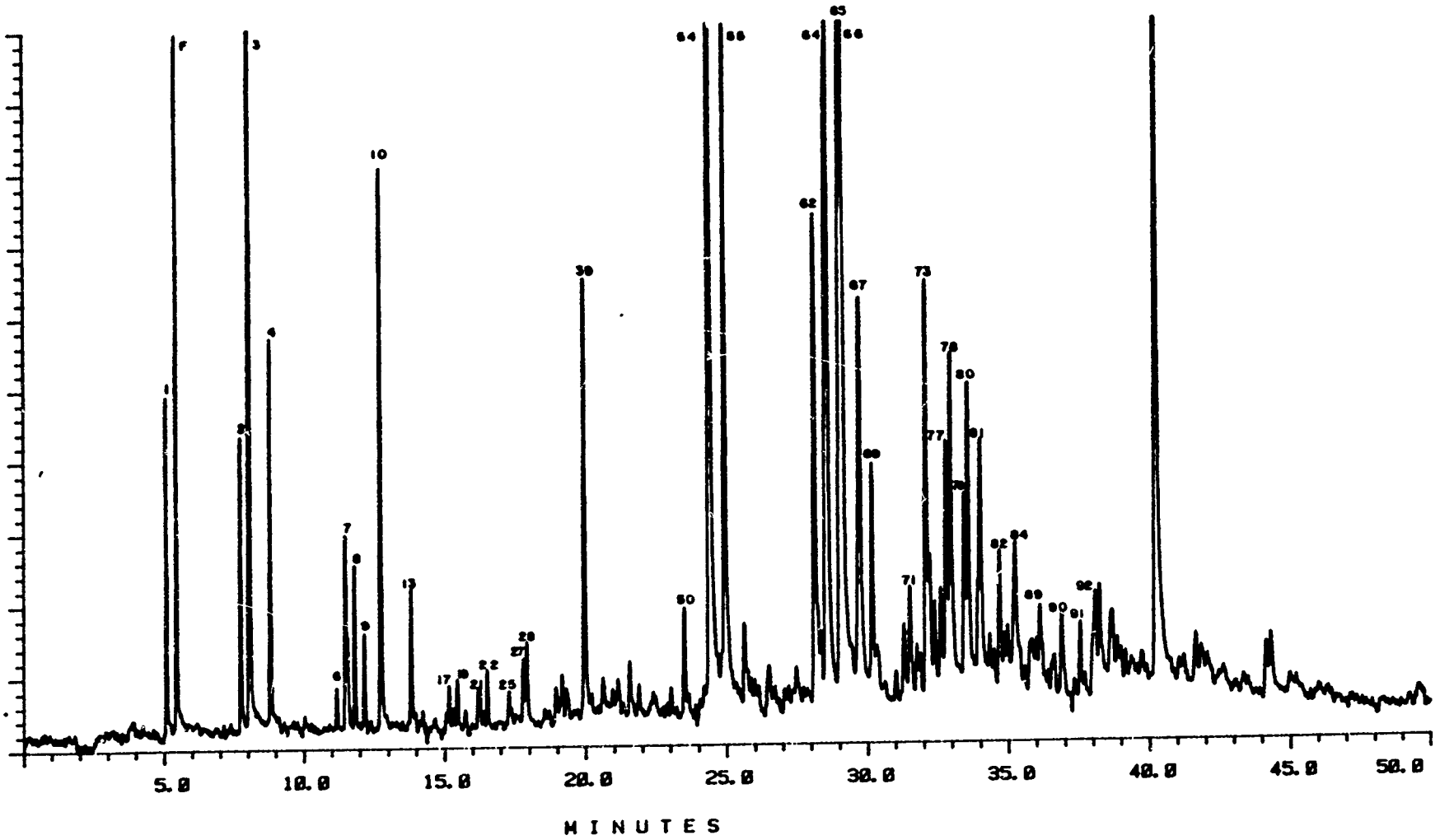


Figure C-20. GC-UVD Chromatogram of Fuel Sample VN-80-74 Determined by Analysis of a Hexane Solution (See Table 2 for tentative identification numbered components).

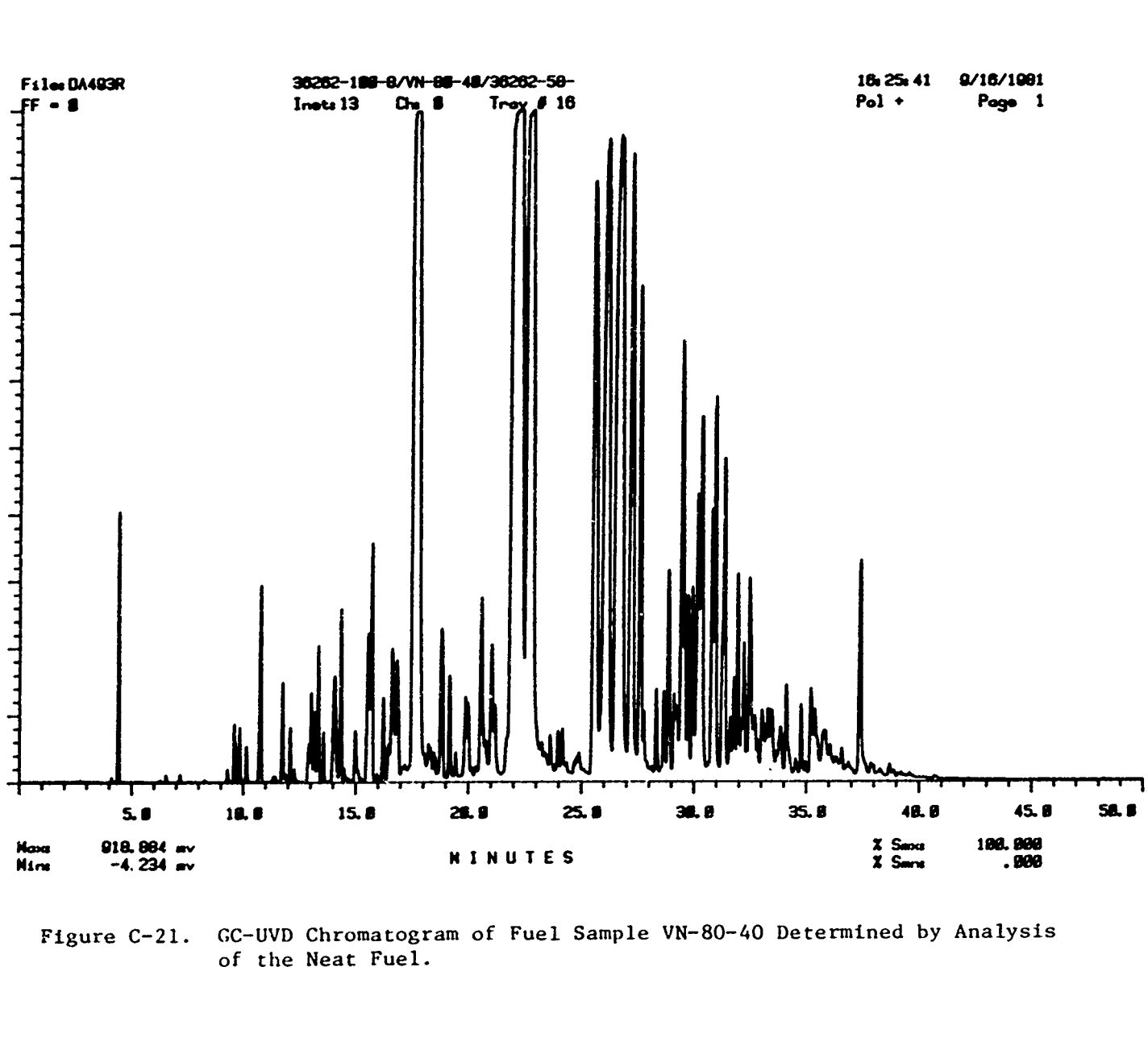


Figure C-21. GC-UVD Chromatogram of Fuel Sample VN-80-40 Determined by Analysis of the Neat Fuel.

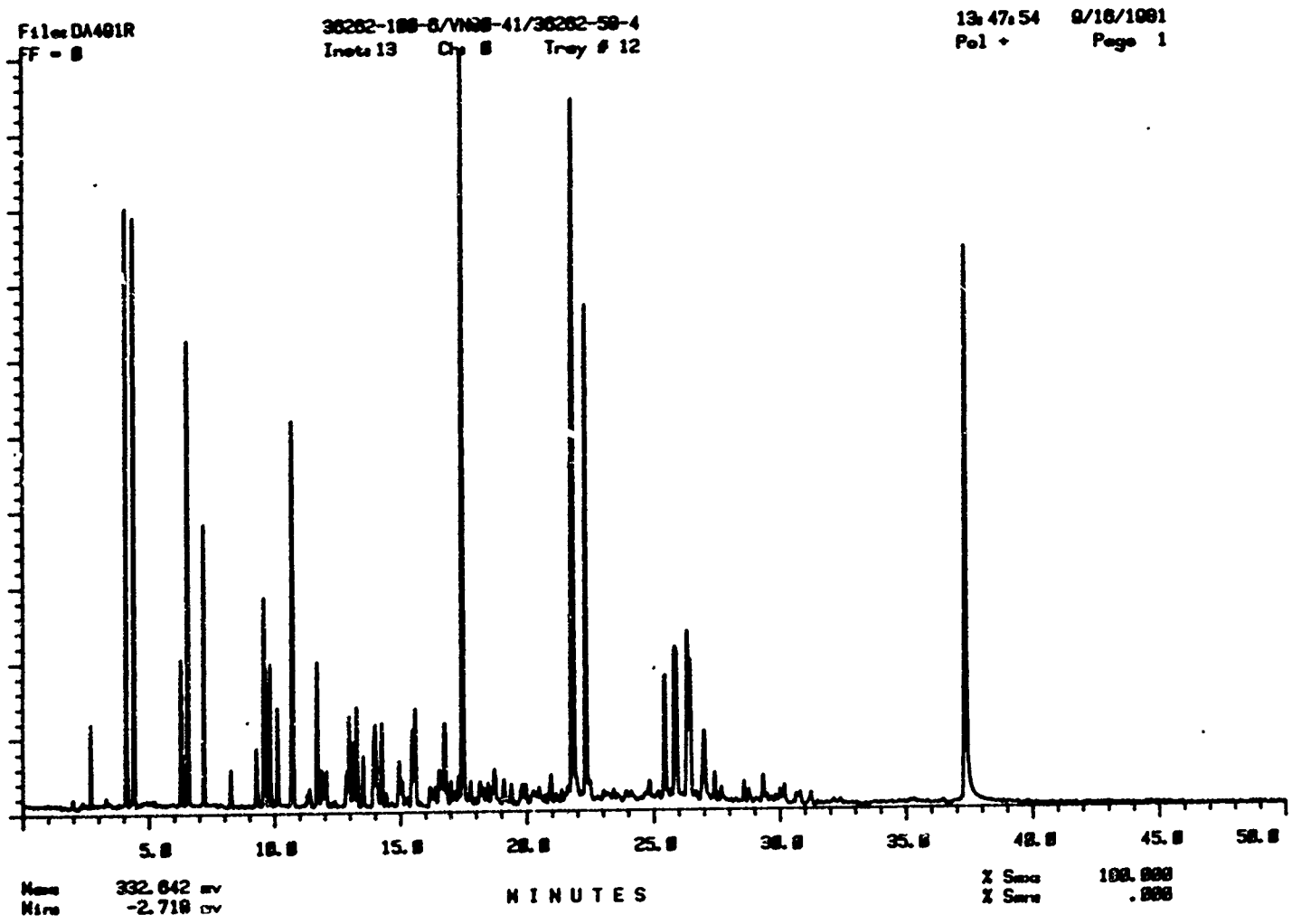


Figure C-22. GC-UVD Chromatogram of Fuel Sample VN-80-41 Determined by Analysis of the Neat Fuel.

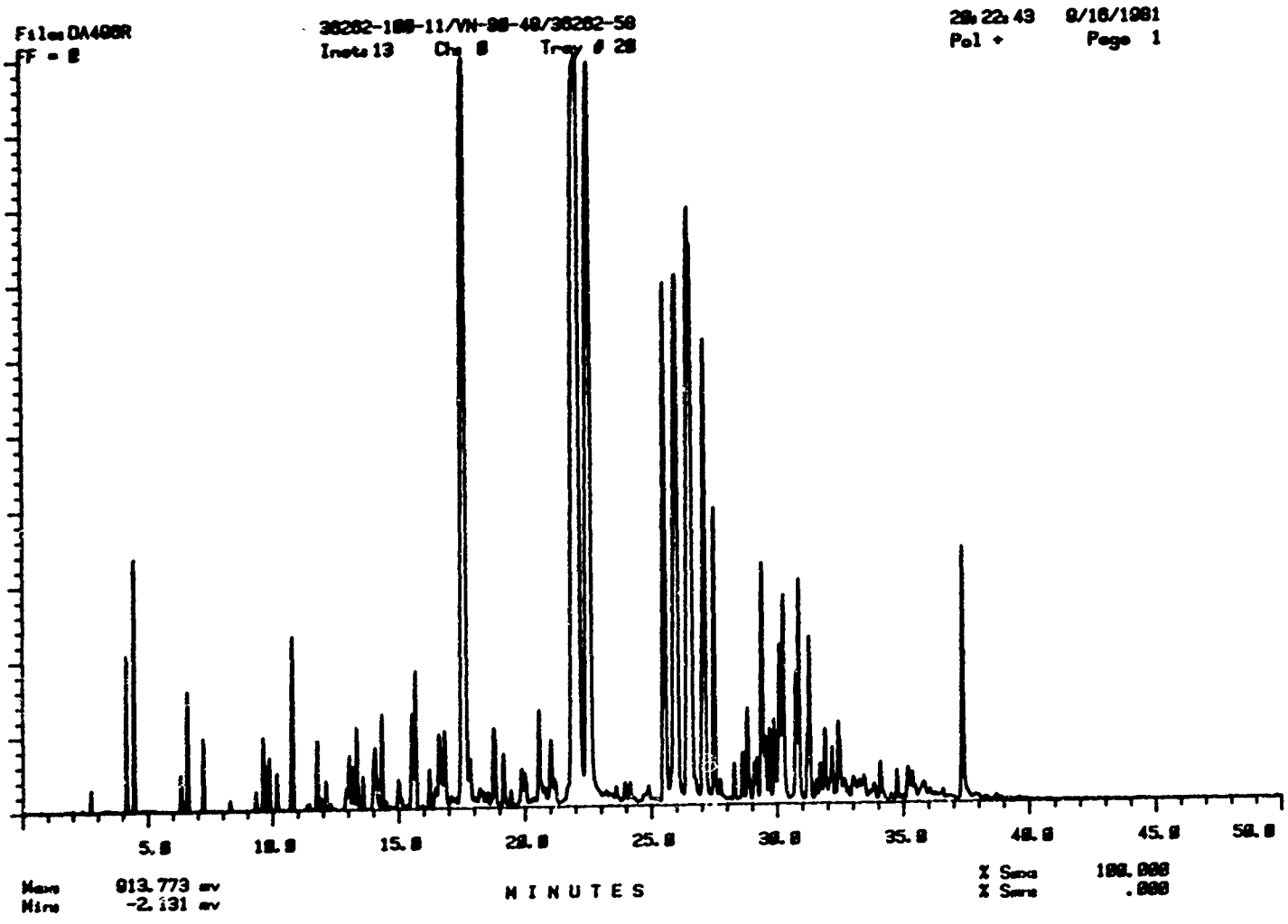


Figure C-23. GC-UVD Chromatogram of Fuel Sample VN-80-48 Determined by Analysis of the Neat Fuel.

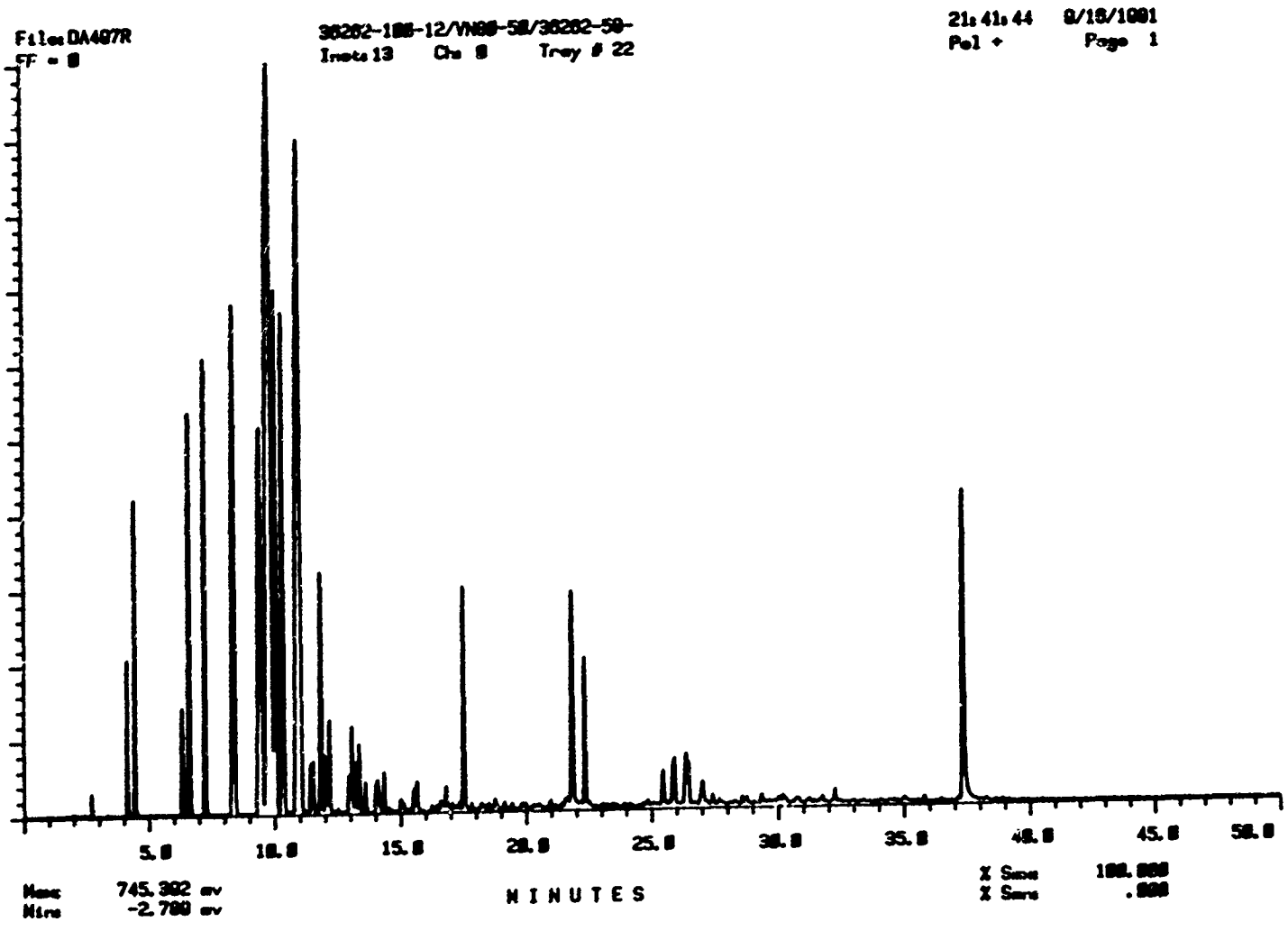


Figure C-24. GC-UVD Chromatogram of Fuel Sample VN-80-50 Determined by Analysis of the Neat Fuel.

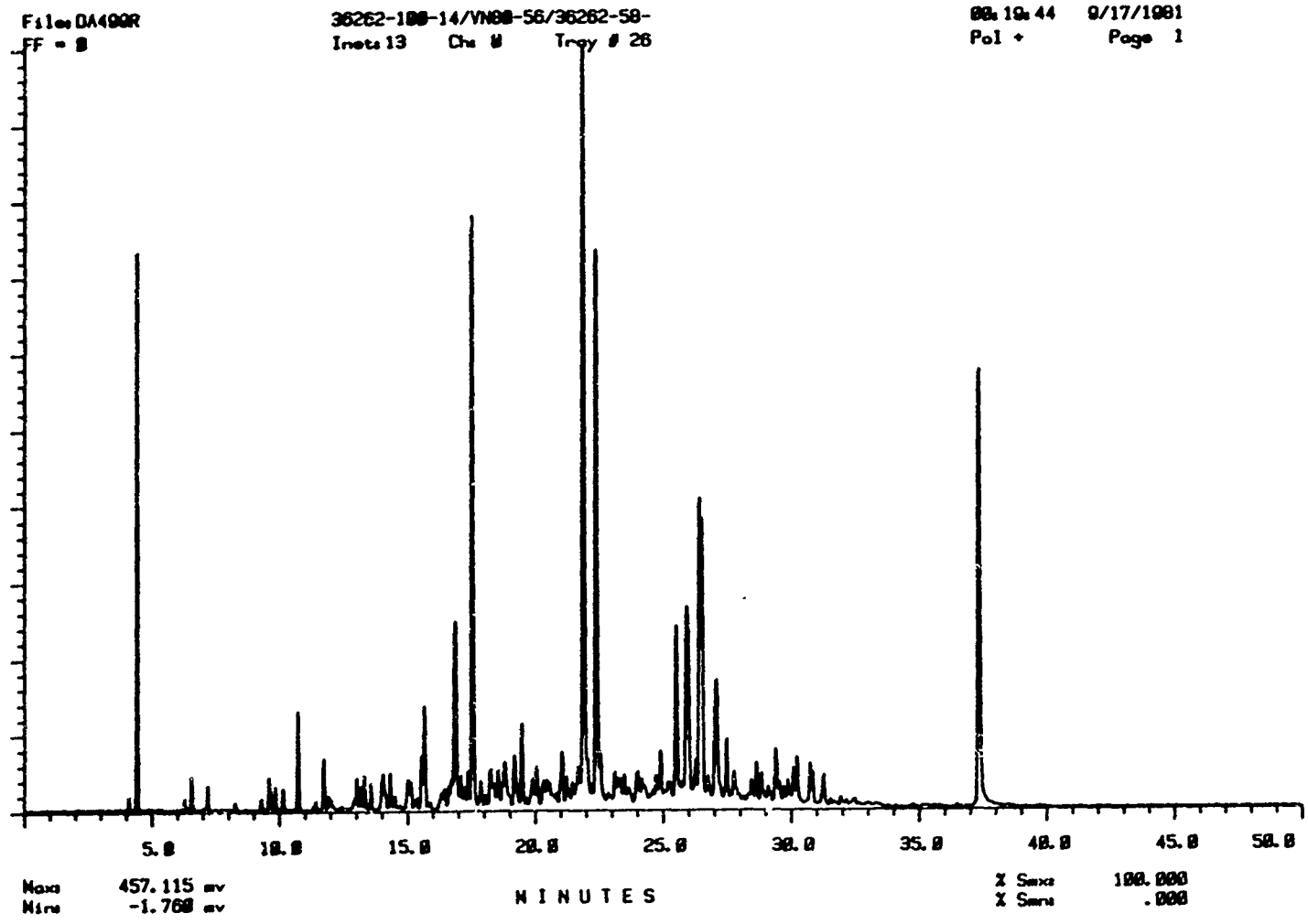


Figure C-25. GC-UVD Chromatogram of Fuel Sample VN-80-56 Determined by Analysis of the Neat Fuel.

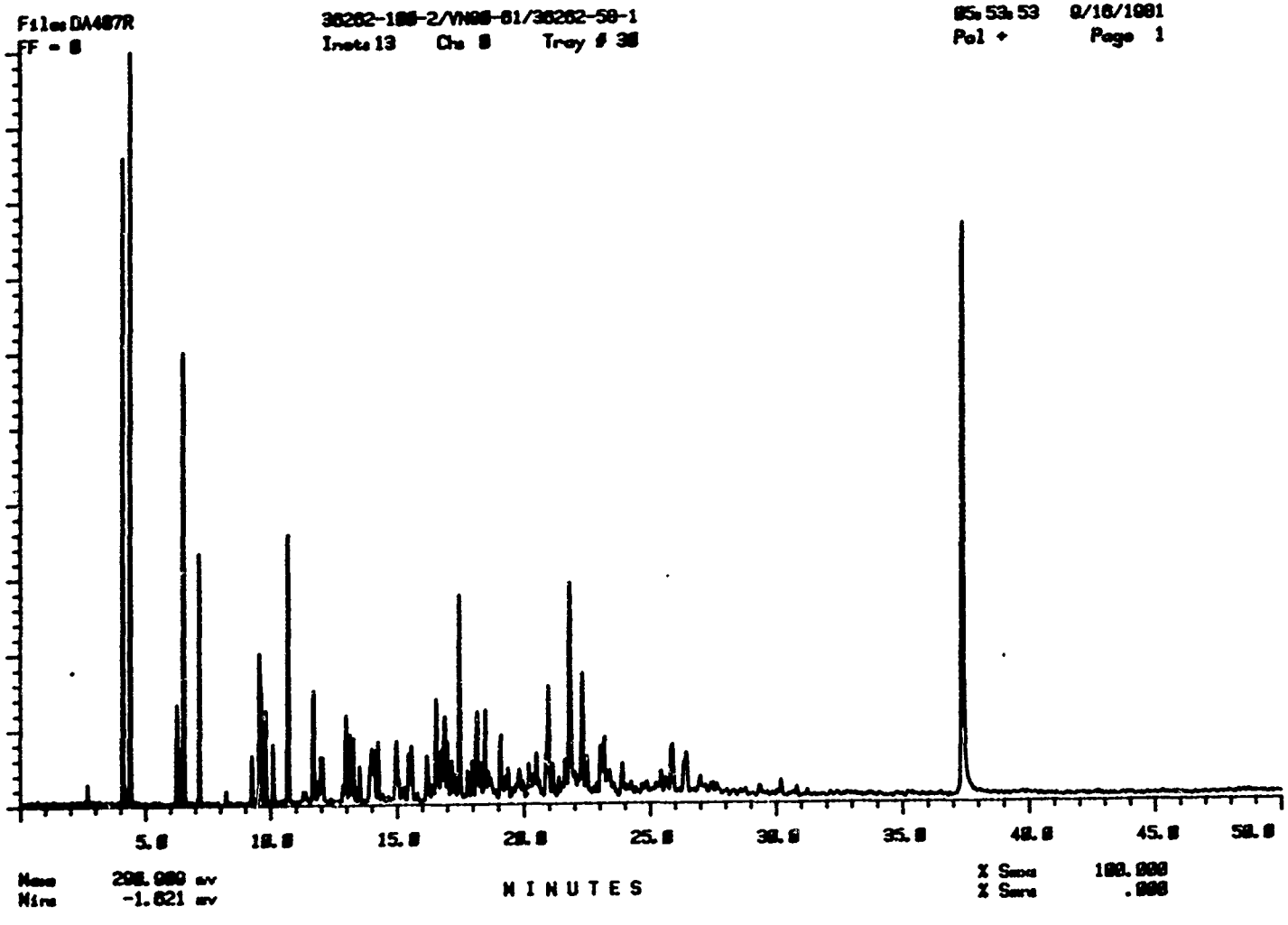


Figure C-26. GC-UVD Chromatogram of Fuel Sample VN-80-61 Determined by Analysis of the Neat Fuel.

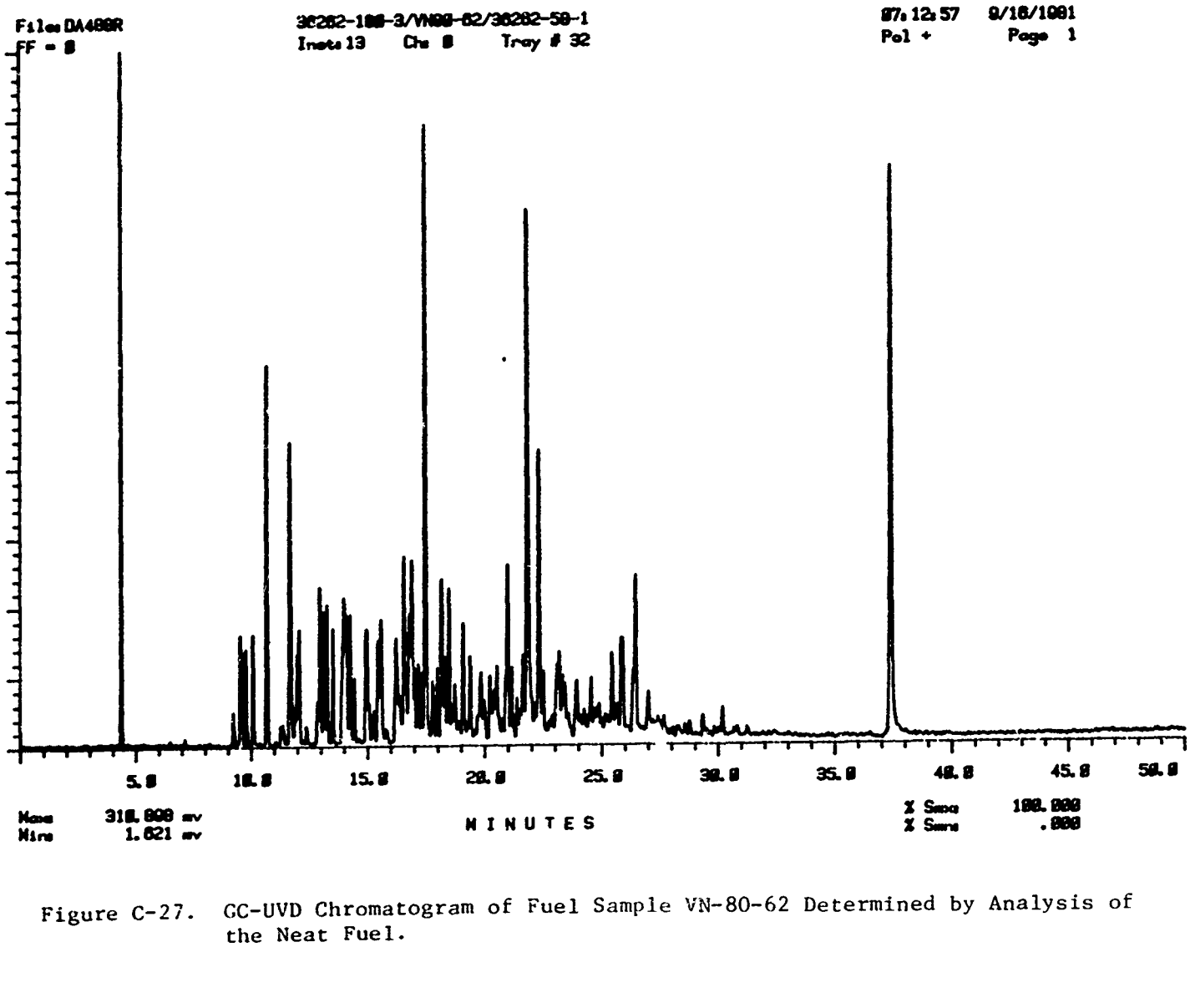


Figure C-27. GC-UVD Chromatogram of Fuel Sample VN-80-62 Determined by Analysis of the Neat Fuel.

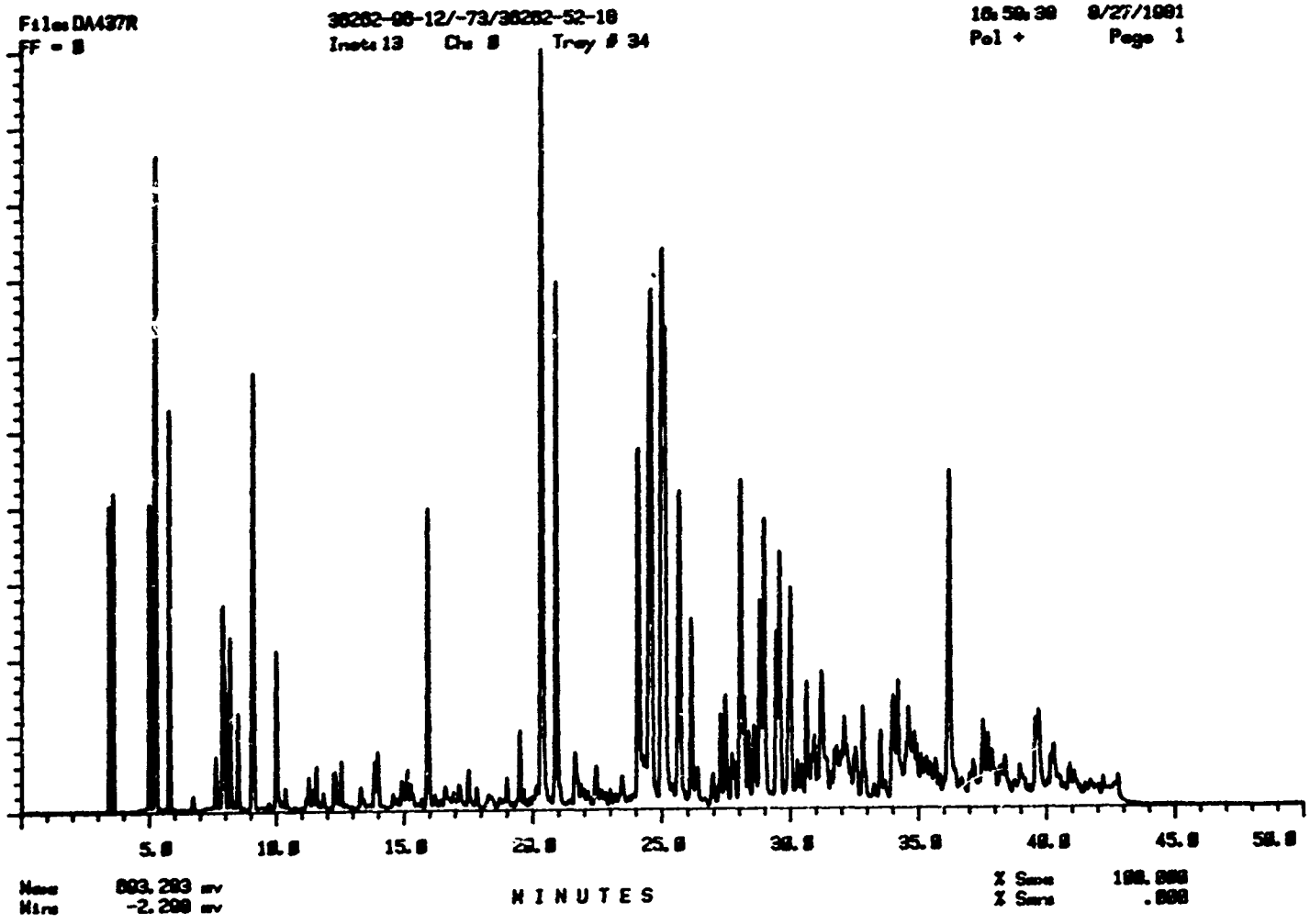


Figure C-28. GC-UVD Chromatogram of Fuel Sample VN-80-73 Determined by Analysis of the Neat Fuel.

APPENDIX D

RECONSTRUCTED GAS CHROMATOGRAMS OF THE BASIC COMPONENTS OF SYNCRUDE JET A

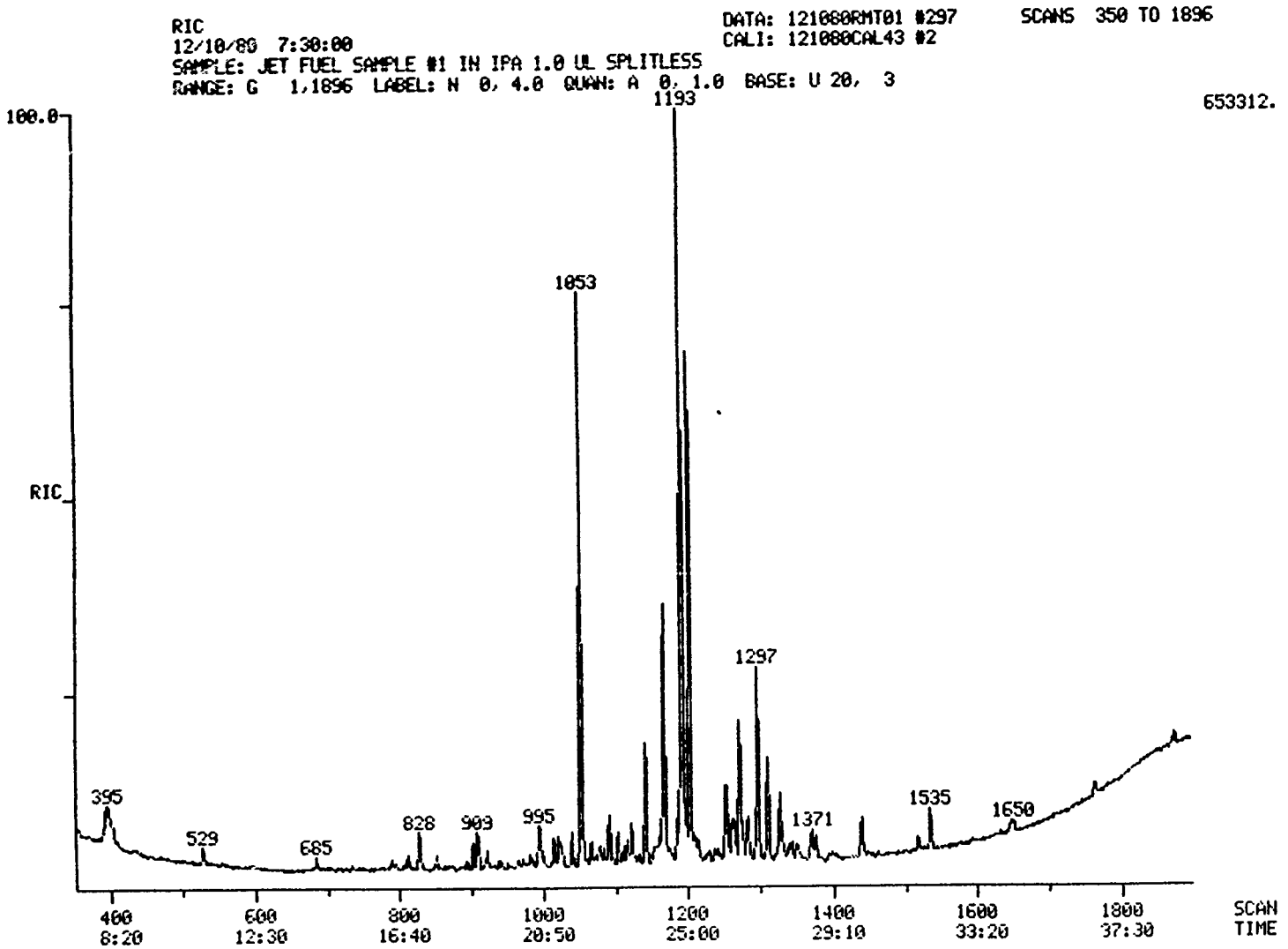


Figure D-1. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 1.

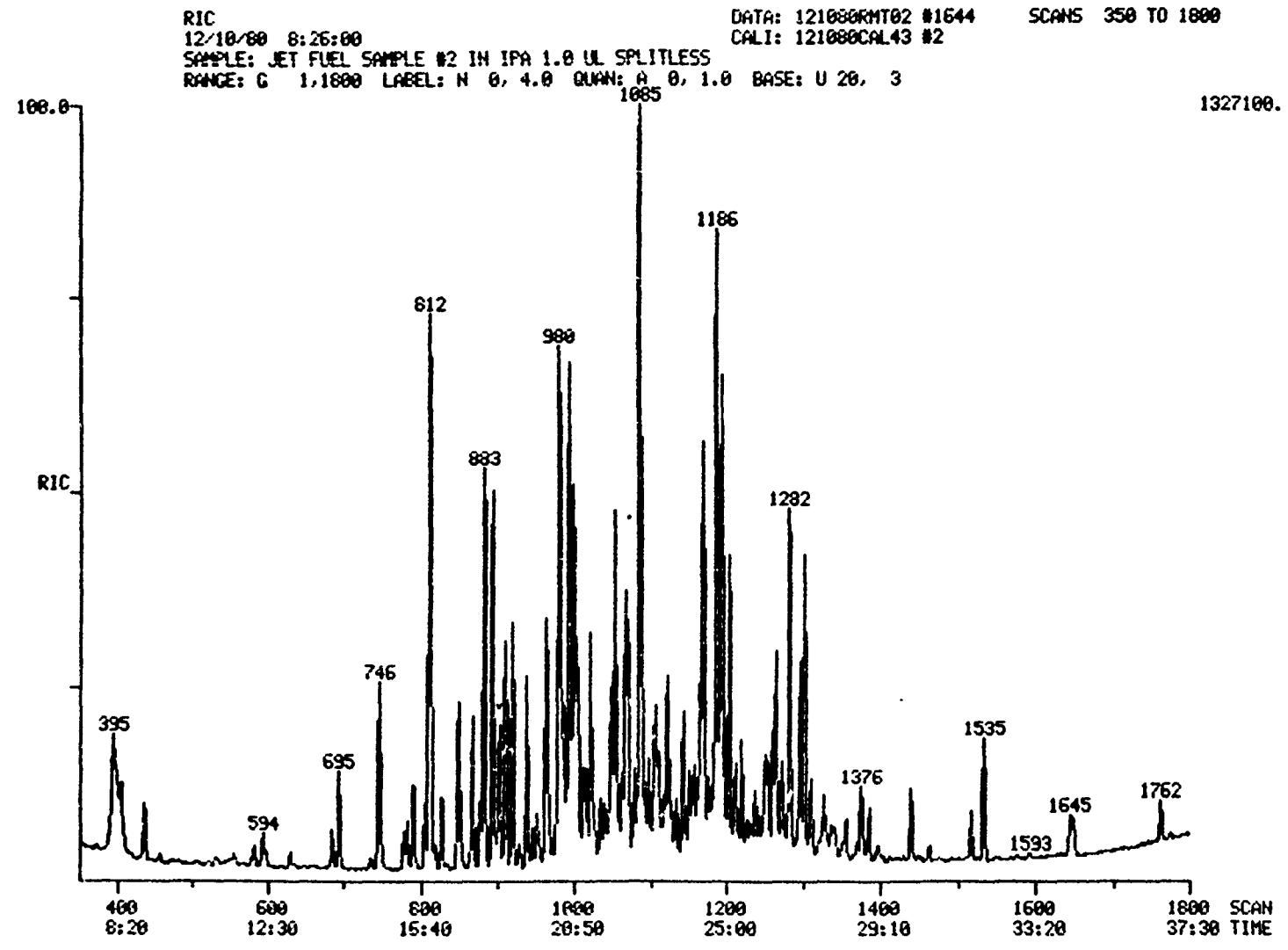


Figure D-2. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 2.

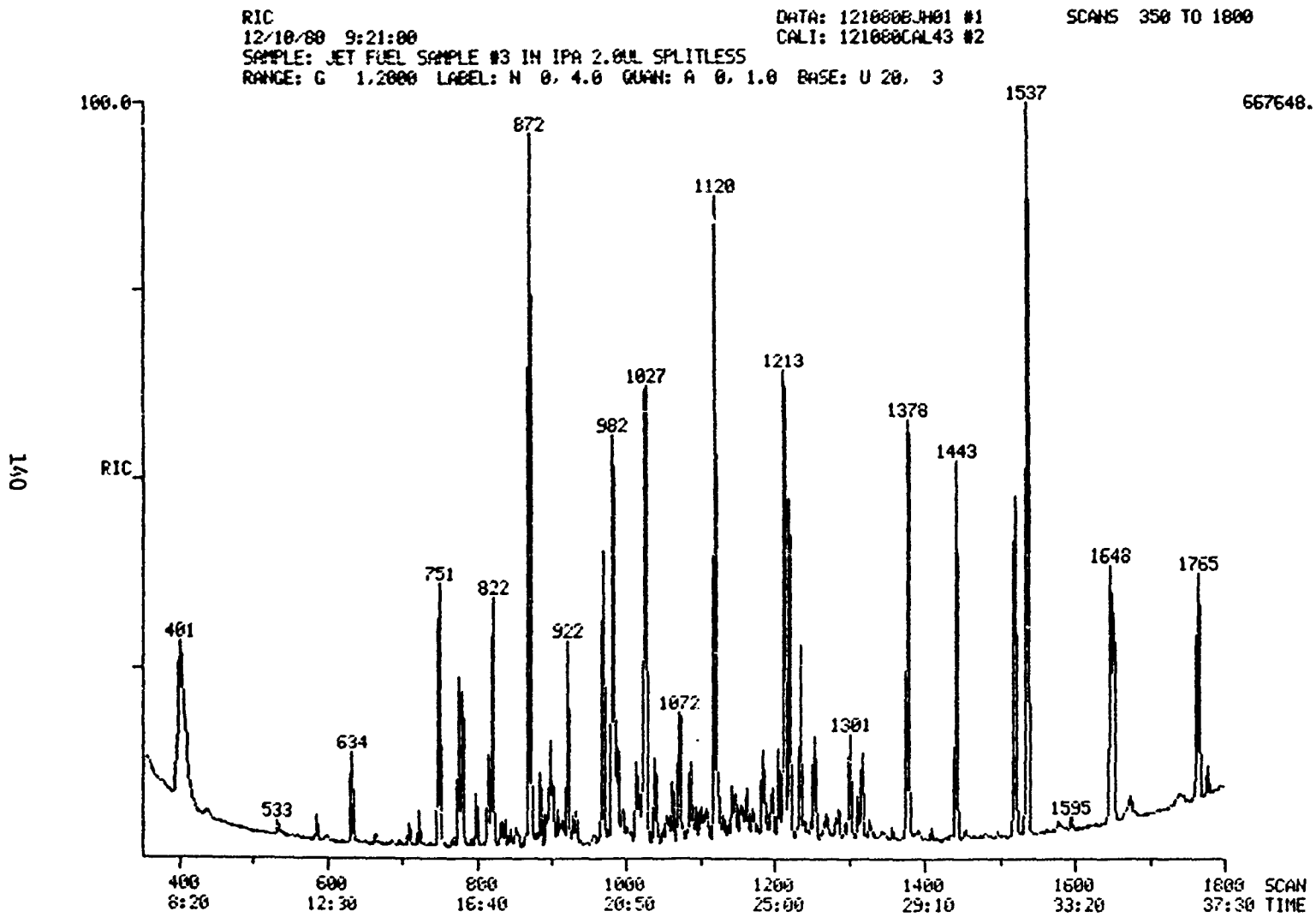


Figure D-3. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 3.

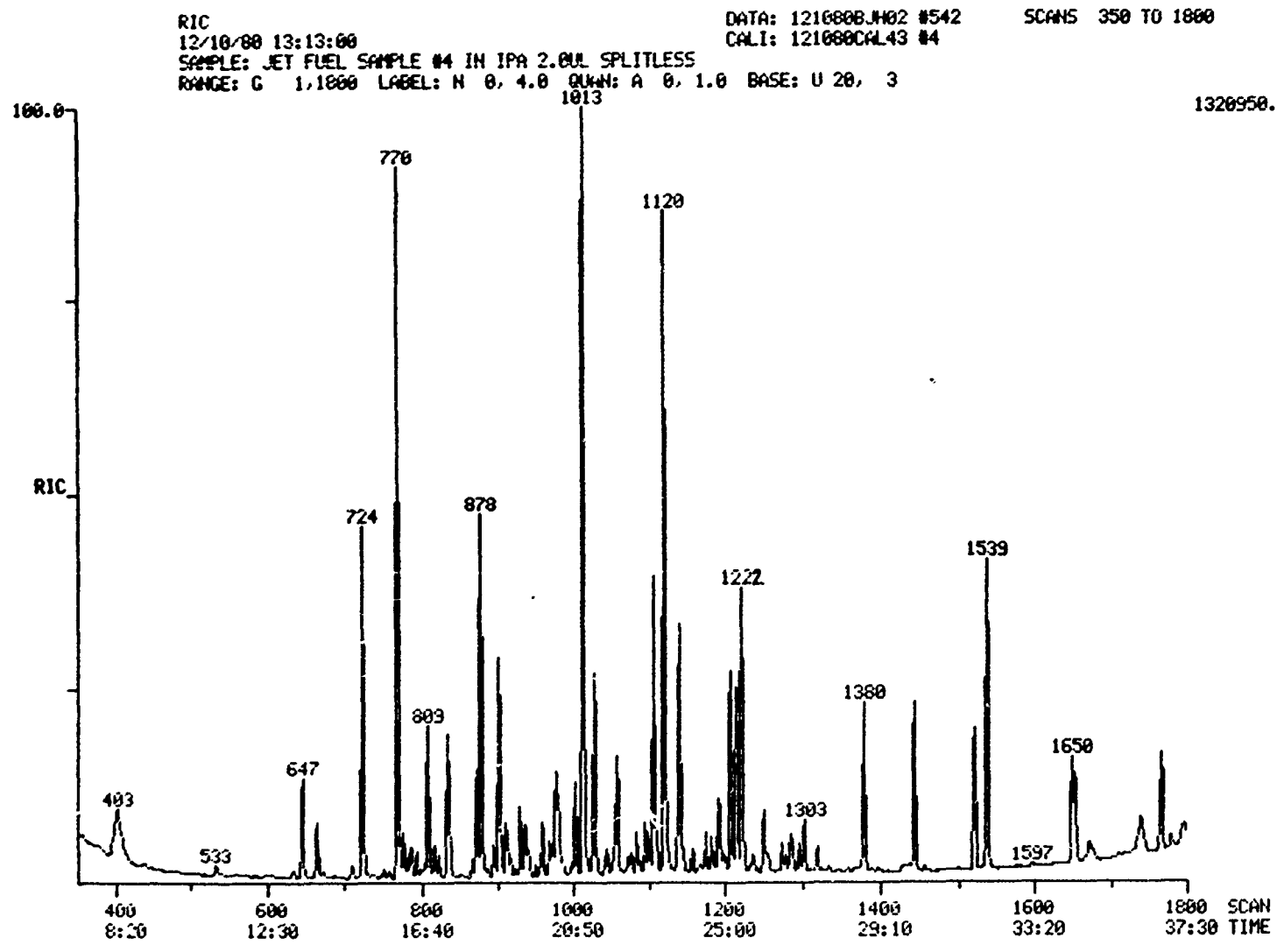


Figure D-4. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 4.

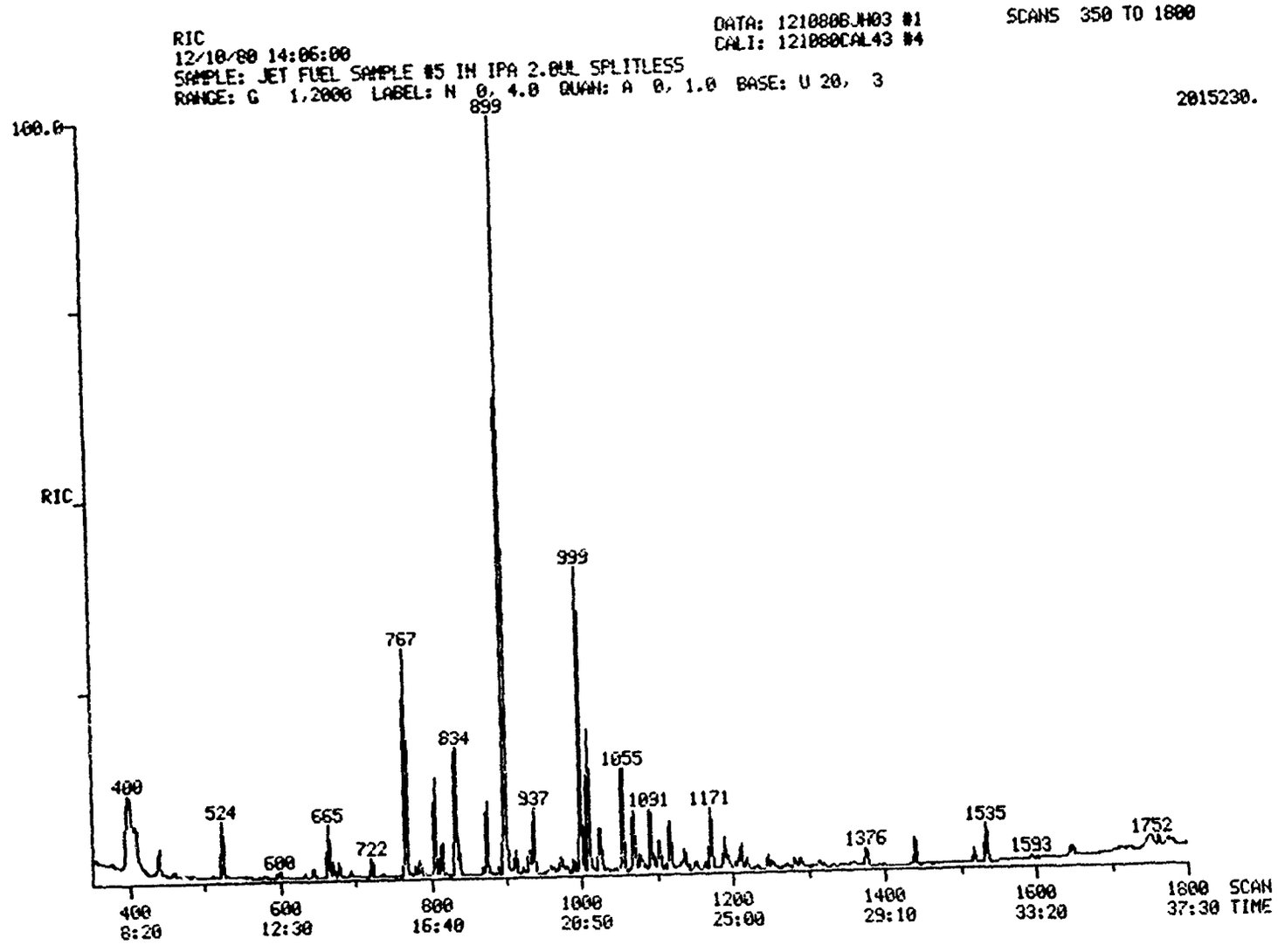


Figure D-5. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 5.

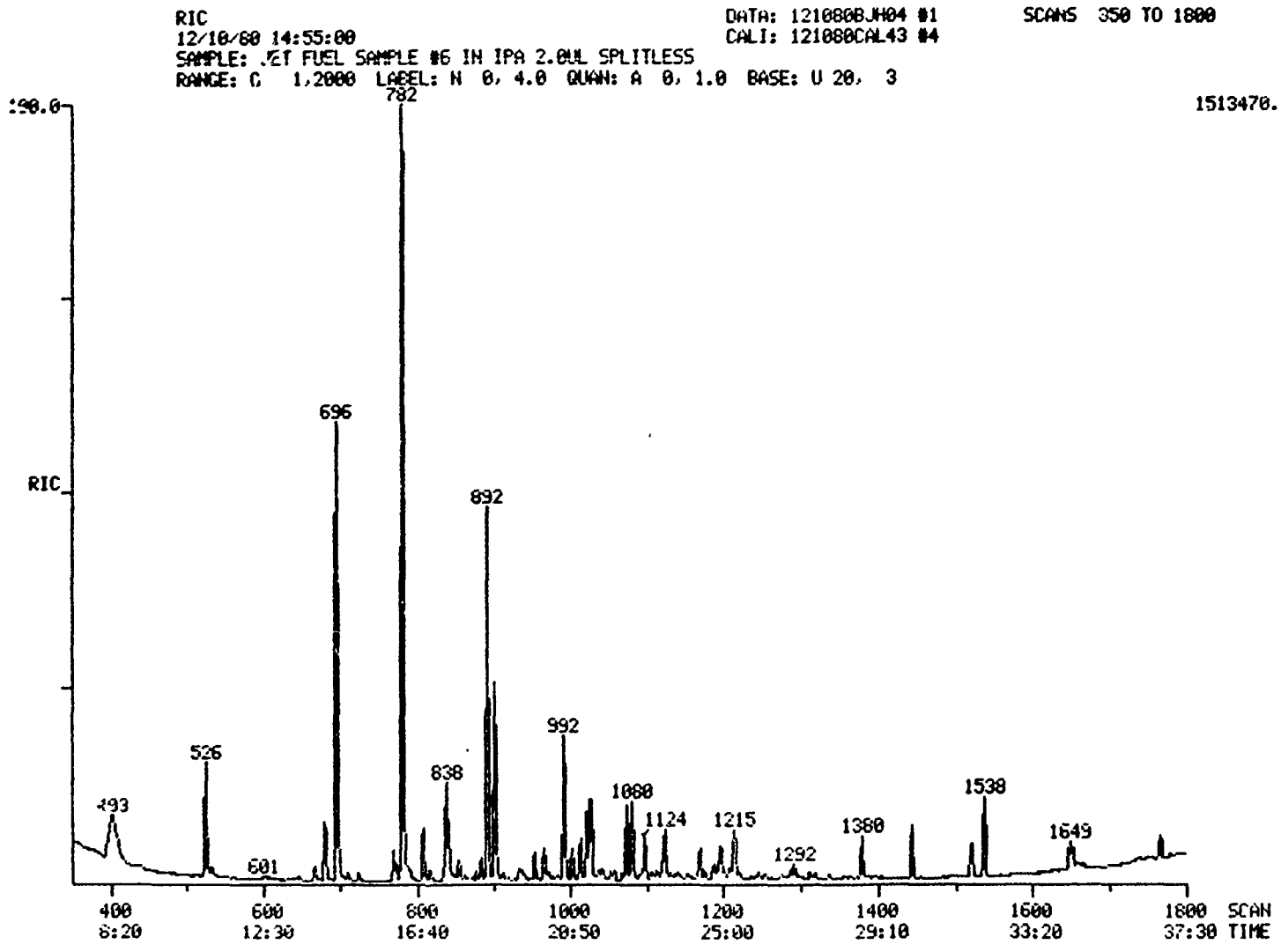


Figure D-6. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 6.

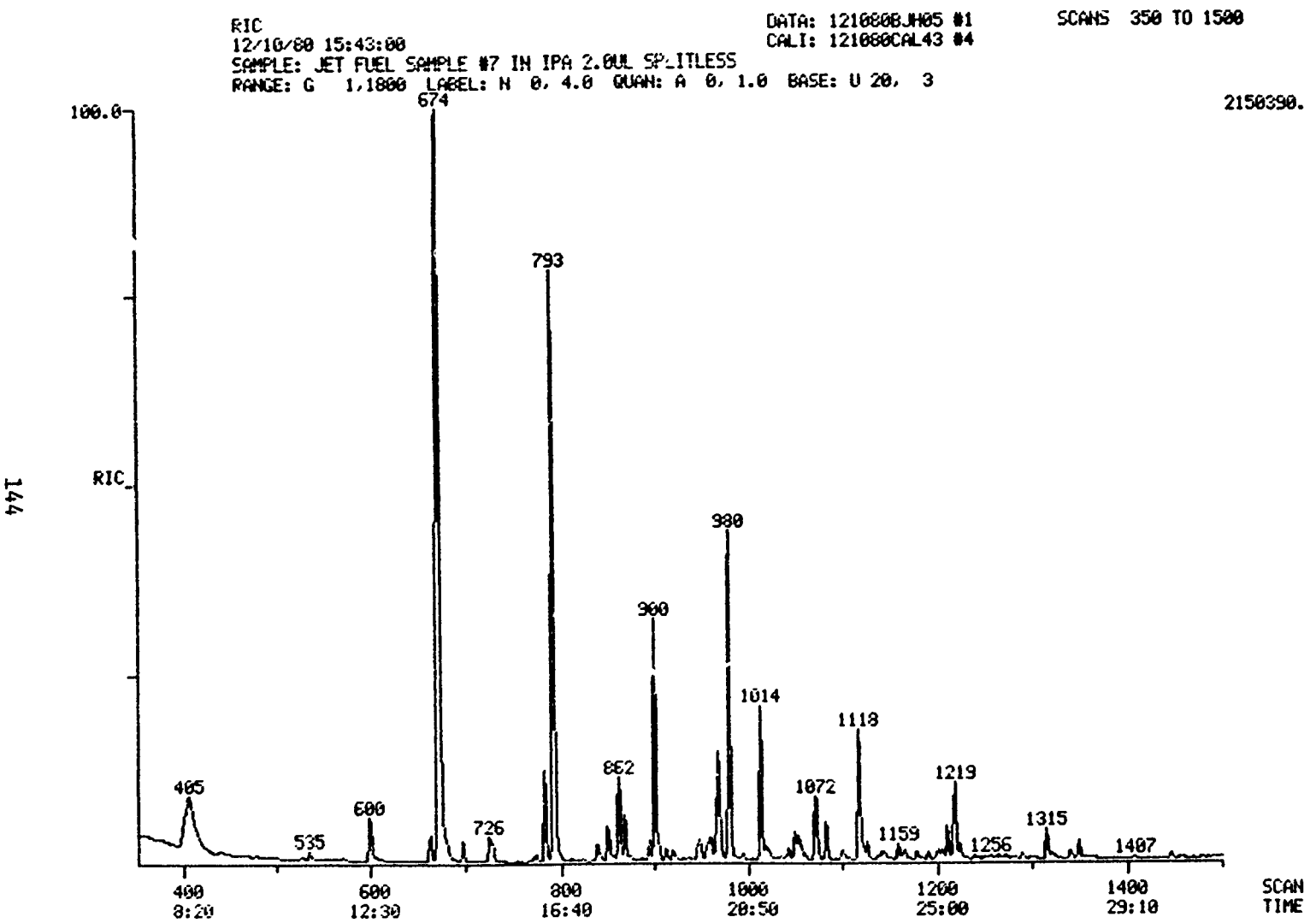


Figure D-7. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 7.

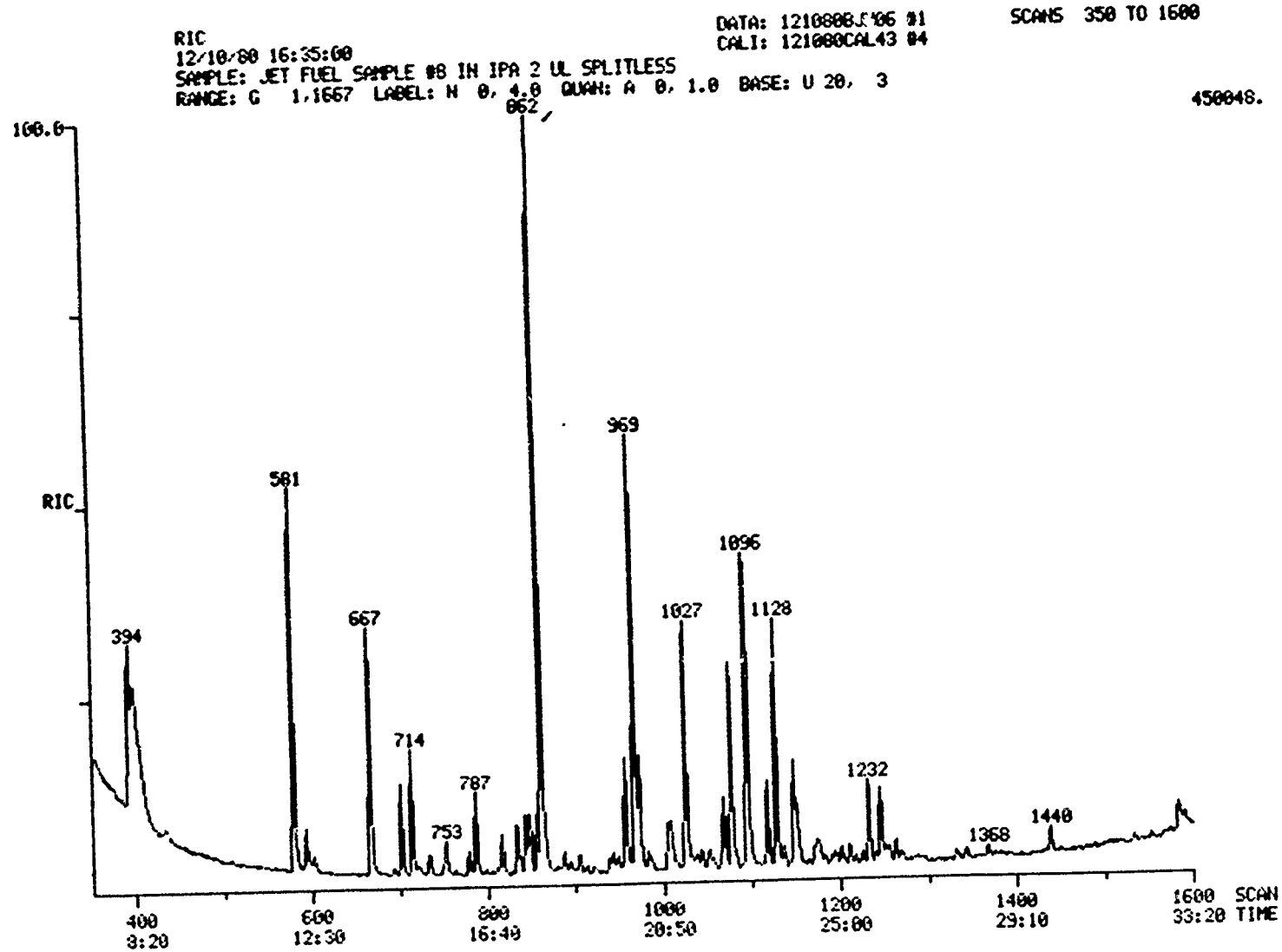


Figure D-8. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 8.

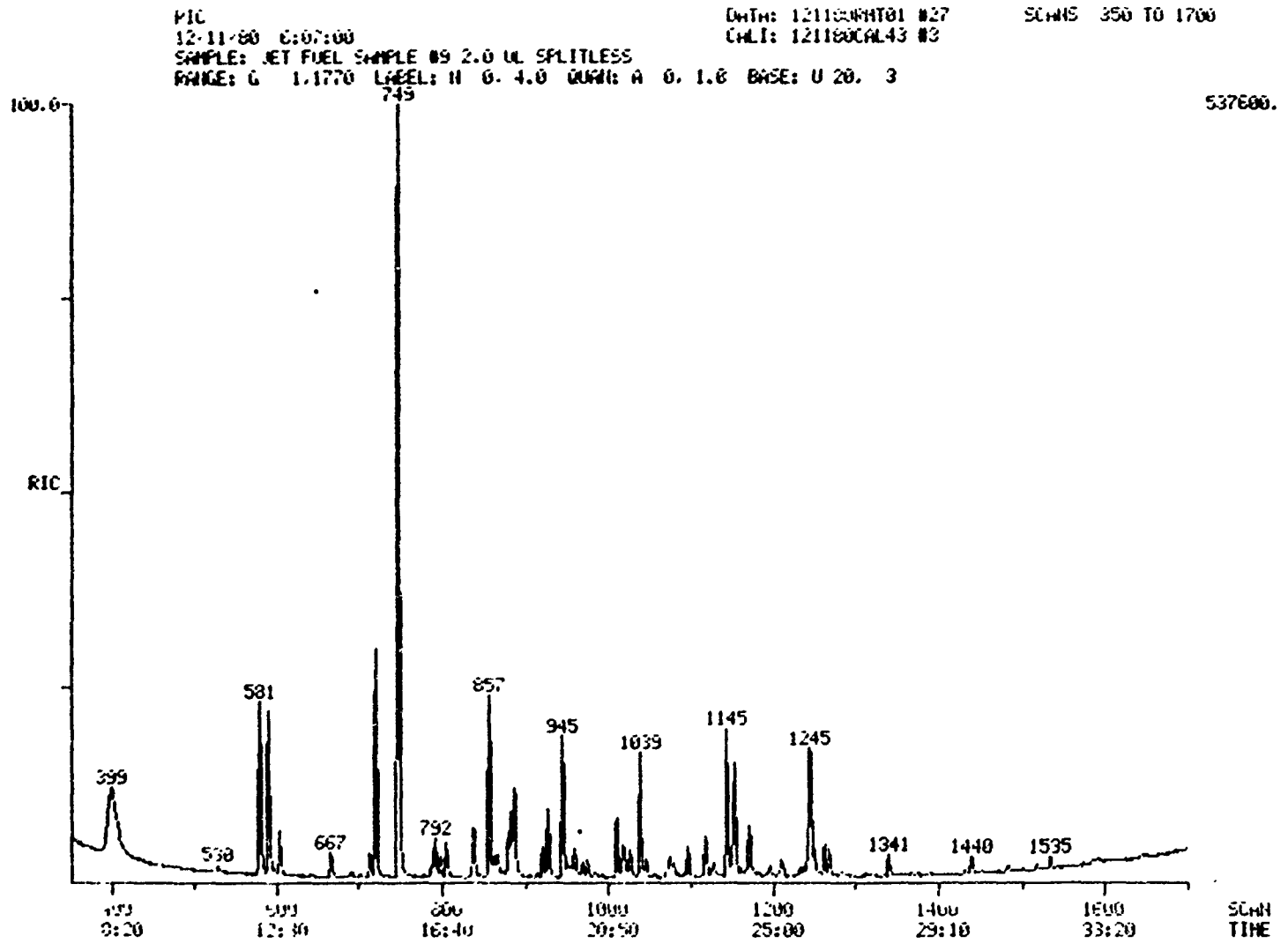


Figure D-9. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 9.

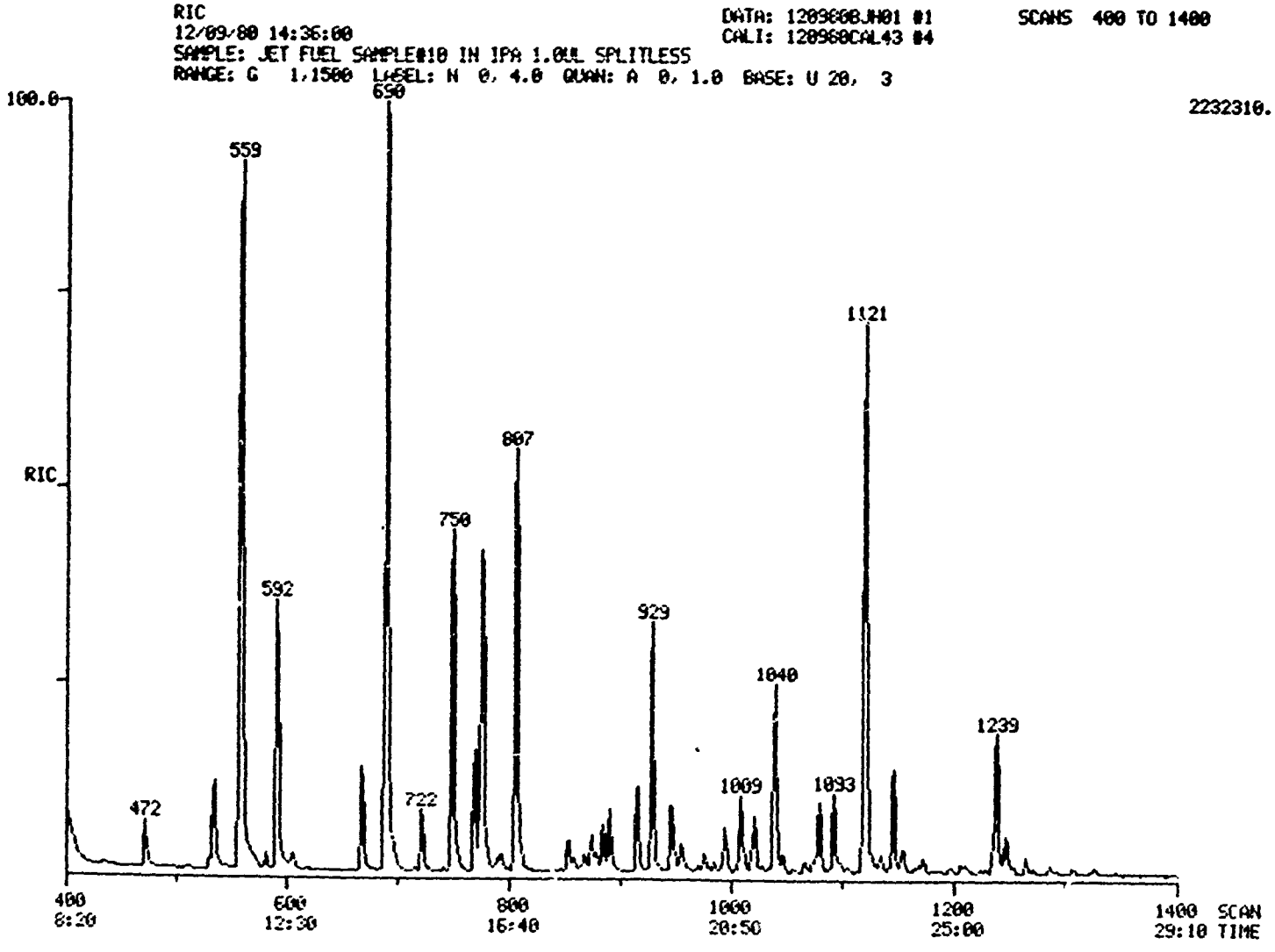


Figure D-10. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 10.

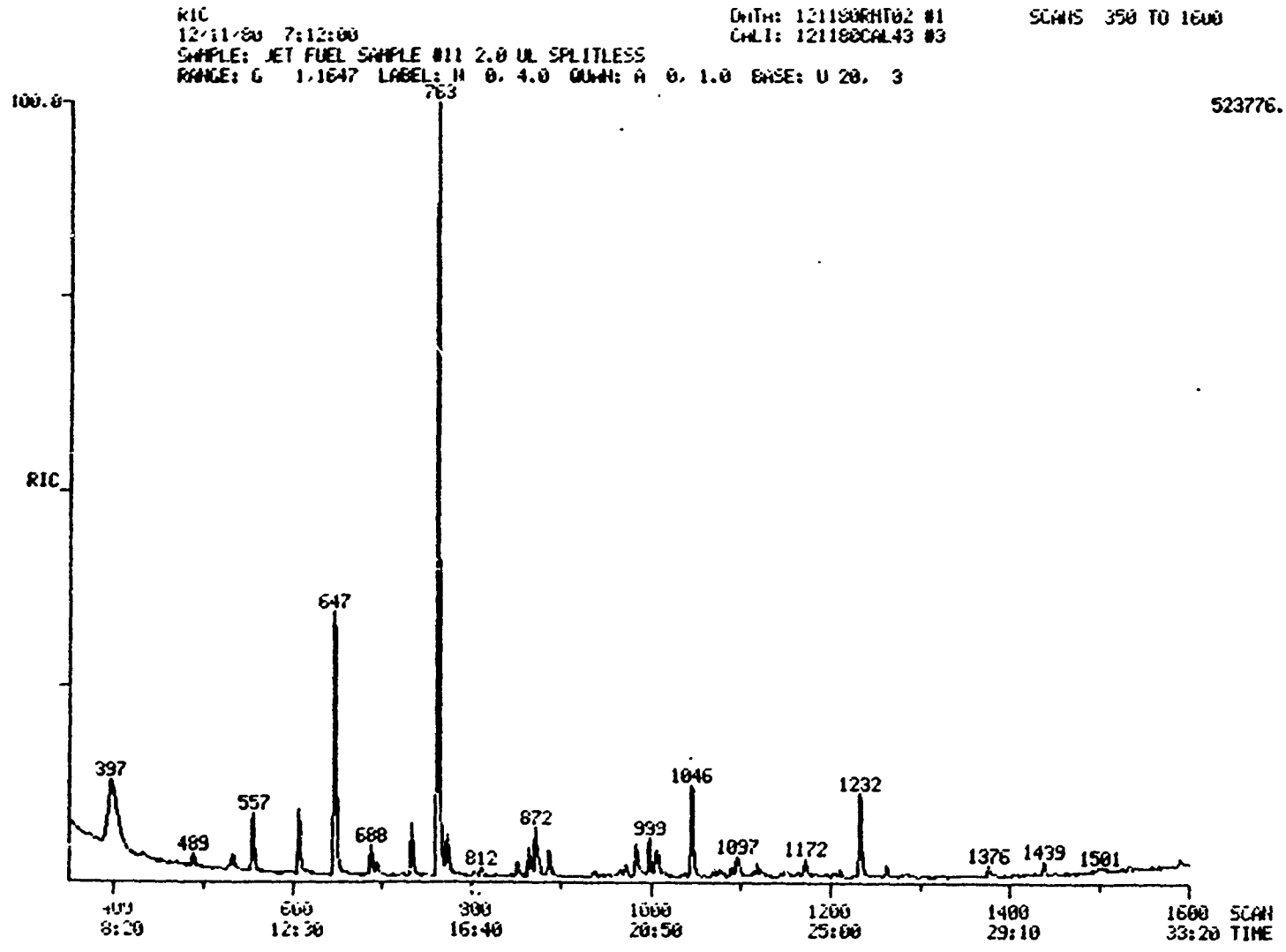


Figure D-11. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 11.

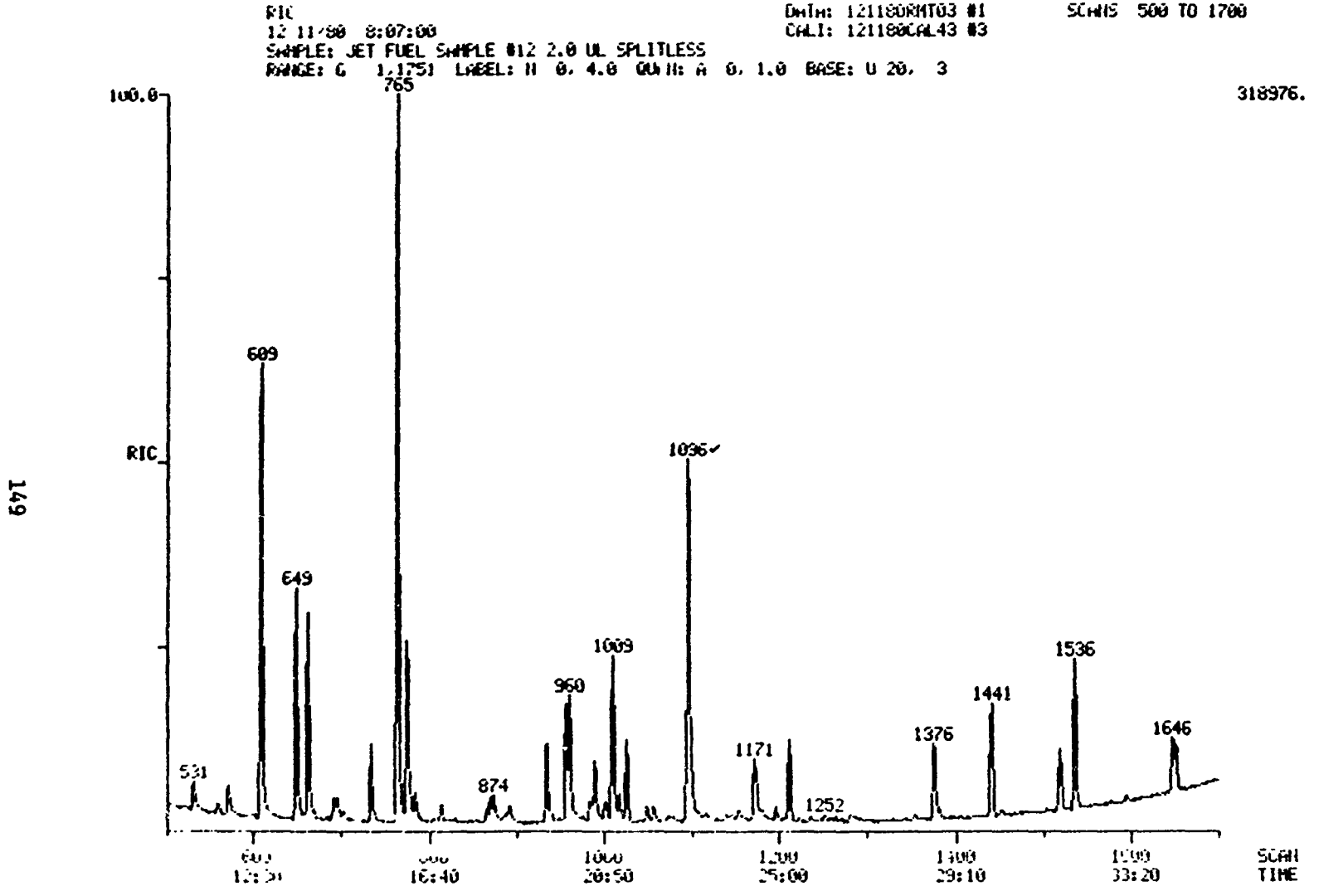


Figure D-12. Reconstructed Gas Chromatogram of the Basic Components of Syncrude Jet A, HPLC Fraction 12.